

# Biogenic Hydrocarbons in the Atmospheric Boundary Layer: A Review



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## ABSTRACT

Nonmethane hydrocarbons are ubiquitous trace atmospheric constituents yet they control the oxidation capacity of the atmosphere. Both anthropogenic and biogenic processes contribute to the release of hydrocarbons to the atmosphere. In this manuscript, the state of the science concerning biosynthesis, transport, and chemical transformation of hydrocarbons emitted by the terrestrial biosphere is reviewed. In particular, the focus is on isoprene, monoterpenes, and oxygenated hydrocarbons. The generated science during the last 10 years is reviewed to explain and quantify hydrocarbon emissions from vegetation and to discern impacts of biogenic hydrocarbons on local and regional atmospheric chemistry. Furthermore, the physiological and environmental processes controlling biosynthesis and production of hydrocarbon compounds are reported on. Many advances have been made on measurement and modeling approaches developed to quantify hydrocarbon emissions from leaves and forest ecosystems. A synthesis of the atmospheric chemistry of biogenic hydrocarbons and their role in the formation of oxidants and aerosols is presented. The integration of biogenic hydrocarbon kinetics and atmospheric physics into mathematical modeling systems is examined to assess the contribution of biogenic hydrocarbons to the formation of oxidants and aerosols, thereby allowing us to study their impacts on the earth's climate system and to develop strategies to reduce oxidant precursors in affected regions.

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## 1. Introduction

Nonmethane volatile organic compounds (NMOCs) represent a key class of chemical species governing global tropospheric chemistry and the global carbon cycle (Fehsenfeld et al. 1992; Singh and Zimmerman 1992). The most important anthropogenic sources of hydrocarbons include fossil fuel combustion, direct release from industry, industrial processing of chemicals, and waste. The global estimated anthropogenic hydrocarbon flux is  $1.0 \times 10^{14}$  gC per year (Singh and Zimmerman 1992). Biological processes in both marine and terrestrial environments contribute to biogenic hydrocarbon sources. For the terrestrial biosphere, the principal hydrocarbon sources come from vegetation. In regions such as eastern North America, biogenic hydrocarbon emission rate estimates exceed anthropogenic emissions (Guenther et al. 1994). At the global scale it is estimated that vegetation emits  $1.2 \times 10^{15}$  gC per year, an amount equivalent to global methane emissions (Guenther et al. 1995).

As shown in Table 1, plants produce a variety of hydrocarbons (Isidorov 1994; Winer et al. 1992; Arey et al. 1991; Guenther et al. 1994). To assess whether biogenic hydrocarbons contribute significantly to the total amount of atmospheric reactive carbon and tropospheric ozone ( $O_3$ ), several interdisciplinary field research programs have recently been undertaken. Examples of these field studies include the Southern Oxidants Study in the southeastern United States (Cowling et al. 1998), the Boreal Ecosystem–Atmosphere Study in northern Canada (Sellers et al. 1995), the Biogenic Emissions in the Mediterranean Area (BEMA) in Italy (Seufert et al. 1997), and the North American Research Strategy for Tropospheric  $O_3$  project in North America (<http://www.cgenv.com/Narsto>). Results from these and other recent field studies have contributed to the development of improved modeling systems to derive regional hydrocarbon inventories and to study the contribution of biogenic hydrocarbons to local and regional oxidant formation. Additionally, recent studies (Mäkelä et al. 1997; Leaitch et al. 1999) have shown the efficient production of carbonaceous aerosols from the photooxidation of NMOCs. Both smog-chamber and field studies reveal that as much as 30%–50% of the submicron aerosol mass is organic matter, and a very significant fraction of this is probably of biogenic origin. While this has been known for some time [a classic paper was published almost 40 years ago by Went (1960)], the important role in global climate forcing has only recently become fully realized (Andreae and Crutzen 1997; Hayden 1998).

In this article we review the generated science to explain and quantify hydrocarbon emissions from vegetation and to discern the impacts of biogenic hydrocarbons on local and regional atmospheric chemistry. In section 2 we report on the physiological and environmental processes controlling biosynthesis and production of hydrocarbon compounds. We outline in section 3 measurement and modeling approaches developed to quantify hydrocarbon emissions from leaves and forest ecosystems. Section 4 includes a synthesis of the atmospheric chemistry of biogenic hydrocarbons and their role in the formation of oxidants and aerosols. Finally, we address in section 5 the integration of biogenic hydrocarbon kinetics and atmospheric physics into mathematical modeling systems to examine the contribution of biogenic hydrocarbons on the formation of oxidants and aerosols, thereby allowing us to assess their impacts on the earth's climate system and to develop strategies to reduce oxidant precursors in affected jurisdictions.

## 2. Controls on biogenic hydrocarbon emissions

Estimating biogenic hydrocarbon emissions relies on empirical models of emissions based on observations. Whenever possible, mechanisms involved in the synthesis and emission of hydrocarbons are used to improve models. Development of mechanistic models of hydrocarbon emissions also improves results when extrapolated to conditions or to regions where empirical data are minimal or unavailable. Mechanistic models are often improved if we understand “why” the compounds are emitted. In this section we review the physiological controls on hydrocarbon emissions.

### a. Biosynthetic pathways

The biochemical pathways involved in synthesis of biogenic hydrocarbons have been the subject of much recent research. Substantially new information has resulted. Here we review the state of the science concerning the biosynthetic pathways for isoprene, monoterpene, and oxygenated hydrocarbons.

#### 1) ISOPRENE

The biosynthetic pathways of the common biogenic hydrocarbons, isoprene, and monoterpenes share a common precursor compound, dimethylallyl pyrophosphate (DMAPP, Fig. 1). This precursor and its isomer isopentenyl pyrophosphate are also precursors for important biological molecules such as carotenoids and cholesterol (Sharkey et al. 1991). This last step in isoprene synthesis is catalyzed by the enzyme isoprene synthase (Fig. 1). Progress has been made recently in understanding the controls acting on isoprene synthase. It appears to be a membrane-bound, light-activated enzyme that catalyzes the elimination of pyrophosphate from DMAPP (Silver and Fall 1991; Wildermuth and Fall 1996). Changes in activity of isoprene synthase are correlated with changes in isoprene emission (Kuzma and Fall 1993).

Isoprene emission rates are affected by the rate at which the precursor becomes available. It had been assumed that the pathway for DMAPP synthesis for isoprene was the same as used for cholesterol synthesis. However, Zeidler et al. (1997) provide evidence that an alternative pathway is used. Given the large amount of isoprene emitted from plants, this novel pathway may handle more carbon for isoprene synthesis than any other compound. While this discovery may eventually lead to a better understanding of what controls the rate of terpenoid biosynthesis, there is no

way yet to measure the activity of this pathway; isoprene emission could end up being a useful tool to study this putative new pathway. The chloroplast localized pathway begins with glyceraldehyde 3-phosphate and a 2-carbon fragment attached to thiamine pyrophosphate. Enzymes that catalyze this transketolase reaction have recently been described and these are the first enzymes known in this new pathway. As more information becomes known about how this pathway is regulated it may be possible to improve the mechanistic aspects of isoprene emission models.

Isoprene emission inventories are made difficult by the fact that not all plants make isoprene, and it has been difficult to predict which plants will emit and which will not. Recent evidence indicates that isoprene may help protect against rapid and frequent high temperature episodes (Singsaas et al. 1997). In addition, isoprene emission are frequently found in less evolutionary advanced plants. In a recent survey, 15 of 16 moss species tested emitted isoprene (Hanson et al. 1999). The ecologically relevant *Sphagnum* mosses emit isoprene at rates similar to oak trees when compared relative to their respective rates of photosynthesis. Isoprene emission is also common among ferns (Tingey et al. 1987). It is common among trees, especially trees with large leaves such as oaks that can heat up in sunlight. Isoprene emission is uncommon among herbaceous and crop plants; this could reflect the fact that many herbaceous and crop plants use large amounts of water to help keep their leaves cool. Isoprene emission has not been found among the cacti. Although cacti are subject to extreme temperatures, the temperatures are consistently high, whereas broadleaf trees encounter more variable conditions. Generally, shade-tolerant plant species do not emit isoprene, thus indicating a light adaptation by plants.

## 2) MONOTERPENES

Monoterpenes are 10-carbon hydrocarbons that are produced from DMAPP and its isomer isopentenyl pyrophosphate (IPP, Fig. 1). The biosynthesis of monoterpenes and other compounds such as carotenoids and steroids can all be envisioned as the successive addition of branched chains, each chain consisting of five carbon atoms. Monoterpenes are synthesized by the head to tail condensation of DMAPP and IPP to form geranyl pyrophosphate (Ruzika 1953). Several of the genes for monoterpene synthase enzymes in mint and conifers have been identified and cloned (McGarvey and Croteau 1995). The presence or absence of monoterpenes in plant tissues

appears to vary at the familial level. Some families, such as *Pinaceae* (e.g., pine, fir, spruce) or *Lamiaceae* (e.g., mint, basil), have high levels of monoterpenes in most of their members. Others such as *Fagaceae* (e.g., oak, beech, chestnut) have only a few species that show any significant levels of monoterpene emission. Because the monoterpene precursor, geranyl pyrophosphate, is essential for plants, it is easy to see how monoterpene emission has arisen multiple times across plant families.

In contrast to the strict light-dependency shown by isoprene emission, monoterpene emissions are usually independent of light. A few species of oaks lack isoprene emission and show light-dependent monoterpene emission. Young needles on conifers can have both light-dependent and temperature-independent monoterpene emission (Seufert et al. 1995).

Temperature is the dominant factor controlling emission rate from any one plant at any one time (Dement et al. 1975). The effect of temperature on emissions matches closely what would be predicted from temperature–vapor pressure curves. The vapor pressure of a particular monoterpene depends on both

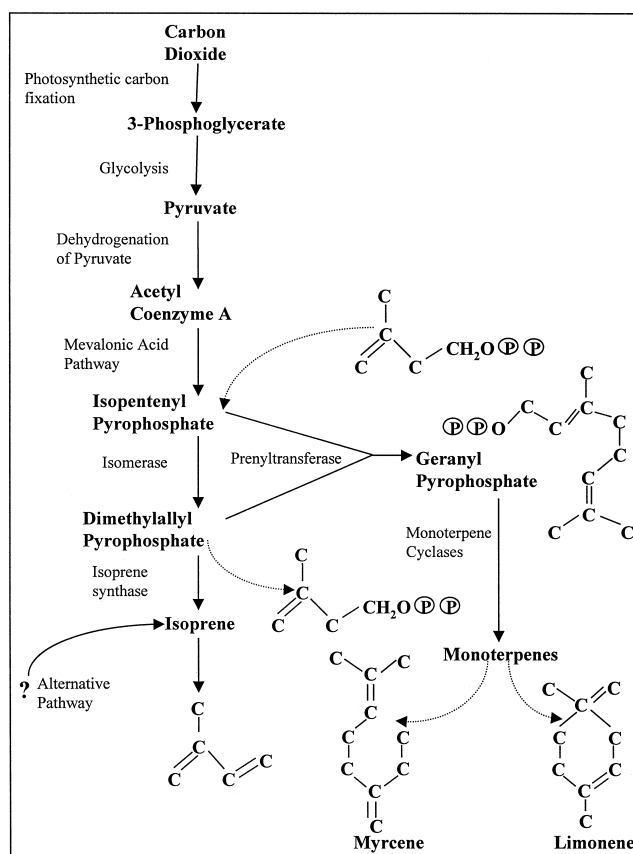
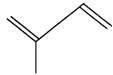








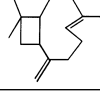
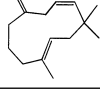



Fig. 1. Biosynthetic pathway for isoprene and monoterpene production in plants.

TABLE 1. Nonmethane organic compounds emitted by vegetation. The molecular weight, boiling point and chemical structure are also presented.

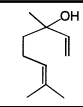
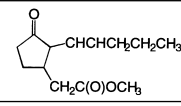










Compound name	Chemical formula	Molecular weight (g mol <sup>-1</sup> )	Boiling point (K)	Chemical structure
Isoprene	C <sub>5</sub> H <sub>8</sub>	68.12	307	
Camphene	C <sub>10</sub> H <sub>16</sub>	136.24	320	
3-Carene	C <sub>10</sub> H <sub>16</sub>	136.24	441	
α-Pinene	C <sub>10</sub> H <sub>16</sub>	136.24	428	
β-Pinene	C <sub>10</sub> H <sub>16</sub>	136.24	436	
Limonene	C <sub>10</sub> H <sub>16</sub>	136.24	448	
Myrcene	C <sub>10</sub> H <sub>16</sub>	136.24	440	
Terpinolene	C <sub>10</sub> H <sub>16</sub>	136.24	459	
Sabinene	C <sub>10</sub> H <sub>16</sub>	136.24	437	
β-Caryophyllene	C <sub>15</sub> H <sub>24</sub>	204.35	396	
α-Humulene	C <sub>15</sub> H <sub>24</sub>	204.35	396	
Methyl chavicol		148.20	489	

its volatility and its concentration in the foliage. Recent studies have shown that the concentrations of the monoterpenes within the plant tissues also affect their emission rates according to a Henry's law relationship; that is, monoterpene emissions increase linearly with concentrations (Lerdau et al. 1994a, 1995).

Unlike isoprene, in most plants monoterpenes are stored in specialized structures. These storage struc-

tures vary with plant taxon and include the glandular hairs on mints; the resin canals found in the needles of pines, *Pinus*; the resin blisters found in firs, *Abies*; the glandular dots in leaves of the citrus family, *Rutaceae*; and the storage cavities in *Eucalyptus* leaves (Lerdau et al. 1997). In the Mediterranean oaks (*Quercus*, section *Sclerophyllodris*), monoterpenes are produced in a light-dependent manner and emitted directly to the atmosphere, without any storage

TABLE 1. *Continued.*

Compound name	Chemical formula	Molecular weight (g mol <sup>-1</sup> )	Boiling point (K)	Chemical structure
Linalool	C <sub>10</sub> H <sub>18</sub> O	154.25	469	
Methyl jasmonate		224.30	383	
Terpinolene	C <sub>10</sub> H <sub>16</sub>	136.24	459	
γ-Terpinene	C <sub>10</sub> H <sub>16</sub>	136.24	455	
α-Terpinene	C <sub>10</sub> H <sub>16</sub>	136.24	447	
β-Phellandrene	C <sub>10</sub> H <sub>16</sub>	136.24	446	
α-Phellandrene	C <sub>10</sub> H <sub>16</sub>	136.24	447	
p-Cymene		134.22	450	
c-β-Ocimene		136.24	373	
t-β-Ocimene		136.24	373	
α-Copaene		204.36	397	
α-Cedrene		204.36	534	

(Loreto et al. 1996). This light-dependent emission of monoterpenes is apparently confined to the *Sclerophylloids* oaks and does not occur in other European or North American oaks. For most monoterpene emitters, the general pattern for the production and storage of monoterpenes is that the production/secretory cells are next to the storage structures so that transport distances are minimized. These storage structures and the lack of light-dependent emissions indicate that monoterpene emissions come primarily

from stored pools, independent of ongoing physiological processes.

Monoterpene production has been found in 46 families of flowering plants and all conifers (Lerdau 1991). Some families where monoterpene production is particularly prevalent are the *Pinaceae*, *Lamiaceae*, *Burseraceae*, and *Rutaceae*. Because of their ubiquity in the *Pinaceae*, all coniferous ecosystems have substantial potential to emit monoterpenes. Temperate deciduous forests emit low monoterpene amounts. In contrast,

tropical forests have many monoterpene-producing species, including members of the *Myrtaceae* and the *Burseraceae*.

### 3) SESQUITERPENES

The biosynthesis of these compounds can be envisioned as a further addition of an isoprene unit to the monoterpene compounds. Condensation of DMAPP and IPP to form geranyl pyrophosphate is the key step for their formation. Sesquiterpenes are present in many plants that synthesize other isoprenoids. But they are not detected due to sampling or analysis procedures or slower detection methods than reaction rates because of their relatively low vapor pressures and/or their high reactivity of sesquiterpenes toward ozone. Sesquiterpene emissions have been documented in plants growing in southern California (Winer et al. 1992) and southern and central Europe (Seufert et al. 1997). Identified plant species to emit sesquiterpenes include orange and tobacco. Because no specific determinations have been made on the sesquiterpene leaf content, it is not known in which compartment of plant tissue they accumulate.

### 4) OXYGENATED HYDROCARBONS

In addition to isoprene and monoterpenes, several oxygenated volatile organic compounds are emitted by plants. All plants studied to date emit methanol when their leaves are expanding (Nemecek-Marshall et al. 1995). The mechanism for this emission is not known, but MacDonald and Fall (1993a) suggest that methanol is produced when cell walls expand (Fig. 2), a process during which pectin is demethylated. Many conifers emit large amounts of acetone from their buds (MacDonald and Fall 1993b).

Many other volatile organic oxygenated carbon compounds are emitted but little is known about the biology underlying their production or emission (Isidorov 1994). Two low-molecular weight compounds that are emitted by plants in response to injury and whose biosynthesis have been studied are methyl jasmonate [methyl 3-oxo-2-(2-pentenyl)cyclopentane acetate] and ethylene (Farmer and Ryan 1990). These two are known to induce defensive reactions within the plants that produce them, and it has been suggested that they also can function as signals to other plants (Farmer and Ryan 1990).

Other classes of compounds that result from damage to plants are leaf alcohol and leaf aldehyde (Hatanaka 1993; Lerda et al. 1997; Fall 1999). Leaf alcohol is *cis* 3-hexenol and is formed by the metabo-

lism of linolenic acid, a fatty acid common in membranes (Fall 1999). Hexenol and related compounds give the "green leaf smell" common when a lawn is mowed or when leaf material begins to rot. Hexenol may help protect wounded plants against pathogen attack.

Several conifers, including ponderosa and lodgepole pine, emit methyl chavicol [1-methoxy-4-(2-propenyl) benzene] (Salom and Hobson 1995). This compound elicits the strongest avoidance behavior by bark beetles of any volatile organic carbon compound. Adding methyl chavicol to a tree has been shown to provide protection from bark beetle attack (Hobson 1995). Studies on trees that are resistant or susceptible to bark beetle attack have shown that resistant trees consistently have higher levels of methyl chavicol (Nebeker et al. 1995). This compound may be the single most important volatile compound in terms of plant-herbivore interactions in conifers, but no studies have examined its possible impacts on atmospheric chemistry, and no estimates exist for emission rates from whole forests.

Another important oxygenated biogenic hydrocarbon is methyl butenol [2-methyl-3-buten-2-ol], which has been shown to be abundant over coniferous forests of the western United States (Goldan et al. 1993). Recent studies on loblolly pine (*Pinus taeda*) have demonstrated that methyl butenol is emitted directly from foliage (Guenther et al. 1996; Harley et al. 1998). This compound is extremely reactive with OH though

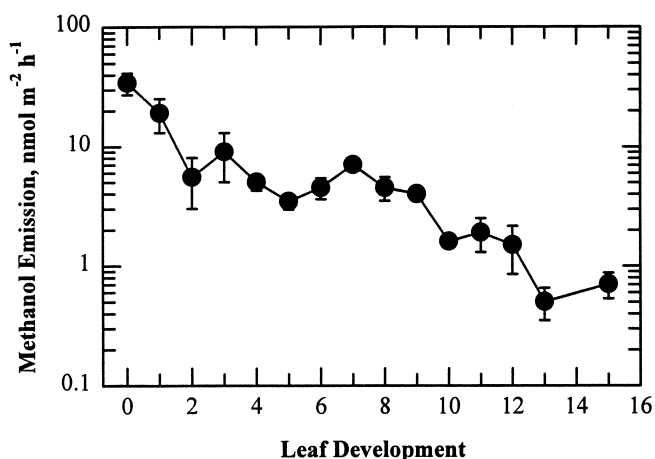


FIG. 2. Relationship between methanol emissions and leaf development in cottonwood (*Populus deltoides*) leaves (adapted from Nemecek-Marshall et al. 1995). Fluxes are expressed per unit leaf area (the conversion of 62 g per m<sup>2</sup> of leaf area was used to convert fluxes from unit dry mass to leaf area). According to Nemecek-Marshall et al. (1995), the leaf development of 0 corresponds to the first unfolding leaf of 32 cm in length and 6 is the first fully expanded leaf.

not with  $O_3$  (Rudich et al. 1995). The high reactivity suggests that methyl butenol may play an important role in atmospheric chemistry by affecting OH concentrations. Arey et al. (1991) have also measured substantial emissions of linalool from orange blossoms of navellate *citrus* varieties. Recent investigations show that the linalool synthase enzyme is responsible for the production of linalool in flowers of *Clarkia breweri* (an annual plant growing in California). Other classes of organic compounds, for which evidence of plant production and emission exist, are the carboxylic acids (Talbot et al. 1988a,b; Lerday et al. 1997).

#### b. Environmental controls on hydrocarbon emissions

In this section we review the principal environmental controls dictating the emissions of hydrocarbons. The discussion applies at the single-leaf level. The best-known environmental control on biogenic hydrocarbon emissions is temperature. For compounds such as monoterpenes that are released from resin ducts or glands, temperature is the dominant control factor (Fig. 3). The increasing vapor pressure of these compounds with temperature explains the temperature response of emissions. In contrast, isoprene and some plant monoterpene emissions do not come from pre-existing pools. In these cases the temperature response of emission is caused by the impact of temperature on the underlying metabolism (Monson et al. 1994). This effect can be described by calculating an activation energy. The activation energy for isoprene emission is relatively constant (Guenther et al. 1993) across a wide range of conditions and most investigators have found similar values ( $60\text{--}90\text{ kJ mol}^{-1}$ ). Although the activation energy is relatively constant, a leaf's capacity to emit isoprene has been found to be variable. The capacity is arbitrarily defined as the rate of emission at  $30^\circ\text{C}$  and  $1000\ \mu\text{mol m}^{-2}\text{ s}^{-1}$ . Figure 4 shows the variation of the emission rate of isoprene as a function of leaf temperature. This measurement was found to vary within a growing season. Also, the temperature of 2–3 days before the measurement could explain much of the variability in basal emission rate. The observed decline in isoprene emissions at leaf temperatures of approximately  $40^\circ\text{C}$  is thought to occur as the enzyme isoprene synthase denatures (Guenther et al. 1993; Fall 1999). Recent data indicate that the temperature at which this occurs can be higher, depending on the growth and developmental environment to which individual plants have adjusted.

Isoprene and some monoterpene emissions are also dependent upon light. The light dependence is often similar to that of photosynthesis, but many reports have shown that isoprene emission can continue to respond to increasing light after photosynthesis is saturated (Fig. 5). The light environment over several days can influence the measured basal rate as found for temperature (Sharkey et al. 1999). Because of the short- and long-term light and temperature responses, isoprene, in particular, will be emitted during hot days with bright light. Because of this, the relative importance of isoprene in atmospheric chemistry and  $O_3$  pollution episodes is even greater than is apparent from global, annual production inventories.

Several environmental factors affect hydrocarbon emission on timescales longer than seconds to days. For isoprene, one of the most significant of these factors is the influence of light environment on isoprene basal emission rate when fluxes are estimated at the plant canopy scale. The light environment affects basal emission rate through impacts on leaf biochemistry and on leaf-specific weight (grams per square meter). Leaves developed in high light environments, such as the leaves at the top of a tree crown, allocate more of their enzymatic machinery to produce more isoprene than leaves developed in shaded environments (Fig. 6). While some of the effect of light environment disappears when fluxes are calculated on a mass basis, there appears to be a residual that can only be explained by biochemical shifts.

Water and nitrogen content affect hydrocarbon emission primarily through their influences on en-

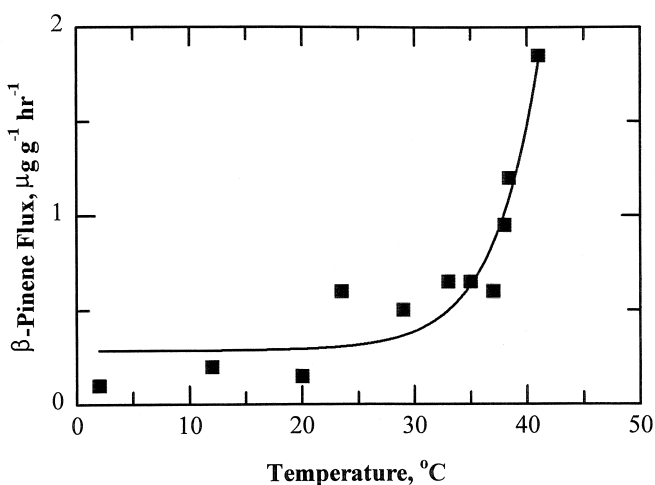


FIG. 3. Variation of monoterpene emissions as function of temperature. The line represents the best fit to the data points. The emission rates are expressed per unit dry biomass weight.

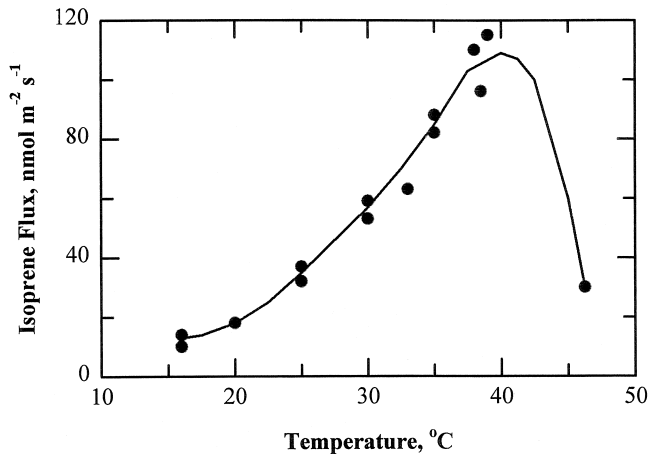


FIG. 4. Isoprene emissions in functions of leaf temperature for white oak (*Quercus alba*) leaves. Fluxes are expressed per unit leaf area.

zyme activity of leaves. Both isoprene and monoterpene emission tend to be highly correlated with the availability of nitrogen. Figure 7 shows a linear relationship between isoprene emissions and nitrogen content in aspen and oak leaves. Positive correlations between isoprene emission rates and leaf nitrogen concentration support the existence of a mechanism linking leaf nitrogen status and isoprene synthase activity (Litvak et al. 1996). The impact of water availability is more complex because, even though isoprene emission declines with water availability (Lerdau and Keller 1997; Fang et al. 1996), transpiration declines even faster, so leaf temperature rises. The overall effect of a decline in water availability is often an increase in isoprene emission because of increased leaf temperature. Upon relief of water stress, plants can

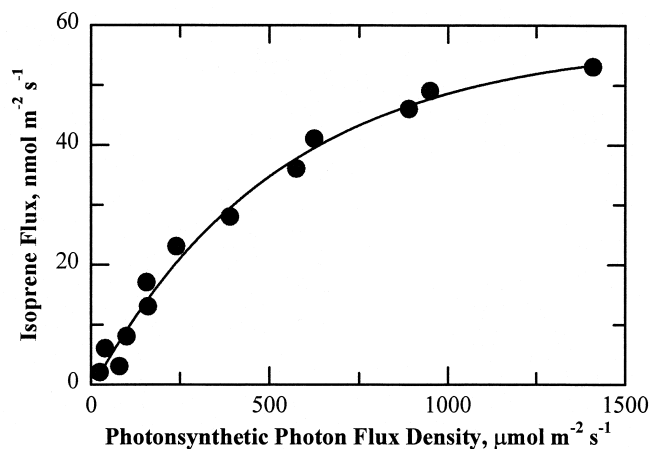


FIG. 5. Isoprene emissions from white oak (*Quercus alba*) and sweet gum (*Liquidambar styraciflua*) leaves in function of photosynthetic photon flux density. Fluxes are expressed per unit leaf area (data from Harley et al. 1996b).

have a higher basal rate of isoprene emission (Sharkey and Loreto 1993). For monoterpenes, water availability is not connected to emission rate (Lerdau et al. 1994a).

Another critical factor controlling hydrocarbon fluxes from leaves is the leaf developmental state. Young leaves that are still expanding do not emit isoprene (Fig. 8), and they do not even possess isoprene synthase (Kuzma and Fall 1993). Fully expanded leaves older than 2–4 weeks, on the other hand, are capable of isoprene emission as long as the leaves have received the requisite period of warm temperatures to induce isoprene synthase activity (Fig. 8). In contrast, monoterpene-emitting foliage shows its highest emission rates when the leaves are youngest (Lerdau 1993). This high emission rate from young leaves results from the role monoterpenes serve as defensive compounds; young leaves are most at risk from pests and pathogens so they have the highest concentrations of defensive compounds (Lerdau et al. 1994b).

The manner in which monoterpenes and several of the oxygenated hydrocarbons (e.g., methyl chavicol) are stored within leaves and wood leads to a large effect of tissue damage upon flux rate. These compounds are stored in specialized ducts, canals, or cavities. When herbivores partially consume tissue and expose these cavities to the atmosphere, flux rates increase by several orders of magnitude. This increase stems from the change in the resistance term in Fick's law of diffusion describing the gas flux (Lerdau 1991). Plants respond to such attacks by secreting nonvolatile com-

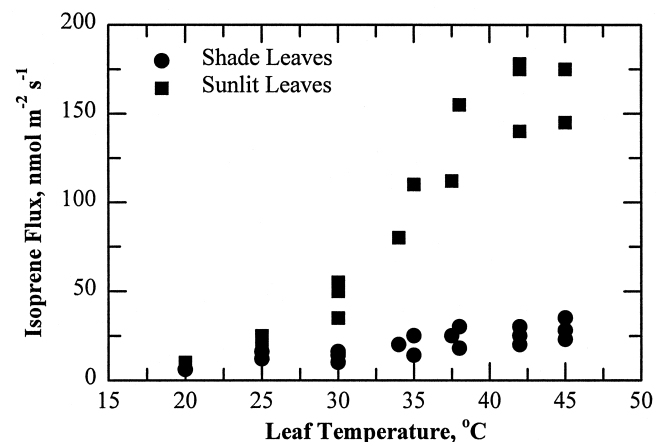


FIG. 6. Isoprene emissions from sweet gum (*Liquidambar styraciflua*) leaves grown at the top of a 22-m canopy crown (sunlit leaves, filled circles) and within the forest canopy (shade leaves, filled squares). At the time of measurements leaves were exposed to light levels near  $1000 \mu\text{mol m}^{-2} \text{s}^{-1}$  (data from Harley et al. 1996b). Fluxes are expressed per unit leaf area.



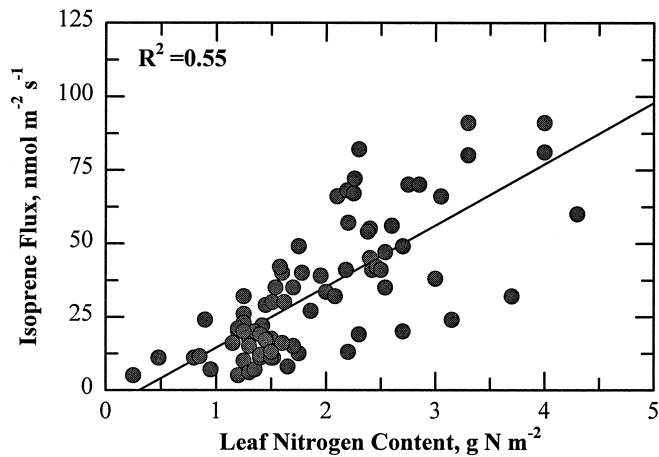


FIG. 7. Emissions of isoprene influenced by leaf-nitrogen content (data from Litvak et al. 1996). Fluxes are expressed per unit leaf area. The line represents the best correlation fit between isoprene emissions and foliage-nitrogen content.

pounds that seal the wounds and cause an increase in the resistance. Recent work, however, has shown that wounding causes an increase in enzyme activity and hydrocarbon biosynthesis that leads to a maintenance of elevated emission rates, even as wounds heal (Litvak 1997). Wounding has been shown to depress isoprene emission rate on the timescale of minutes, but these effects are not long lasting (Loreto and Sharkey 1993).

Little information is available concerning the effects of a globally changing environment on NMOC emissions. Harley et al. (1996a) found no significant effects of increased UV-B radiation on isoprene emis-

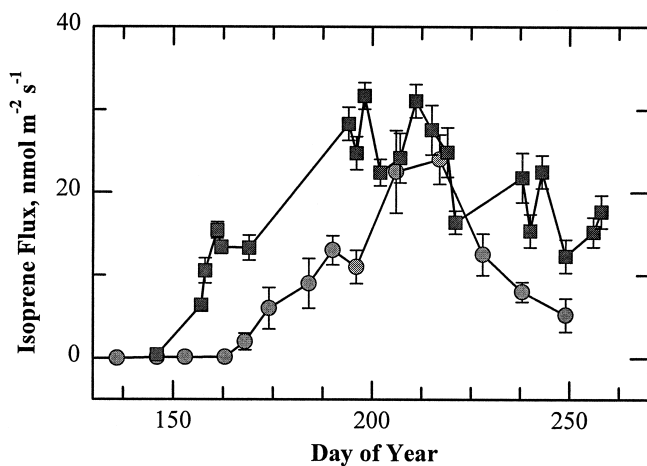


FIG. 8. Seasonal isoprene emissions from aspen leaves [data from Monson et al. (1994), filled circles; data from Fuentes et al. (1999), filled squares]. Fluxes are expressed per unit leaf area (the data represented with filled squares were scaled from the canopy to the foliage level).

sion from *Macuna pruriens* and *Quercus gambelii*. Guenther et al. (1991) also found little change in isoprene emission rates from *Eucalyptus globulus* with changes in carbon dioxide (CO<sub>2</sub>) mixing ratios, except at very high (> 600 ppm) or low (< 100 ppm) levels, where emissions declined by approximately 20%. Monoterpene emissions were insensitive to changes in CO<sub>2</sub> concentration. Sharkey et al. (1991) found a contrasting response by *Populus tremuloides* (30%–40% decrease in isoprene emission with a 60% increase in CO<sub>2</sub>) versus *Quercus rubra* (100% increase in isoprene emission with the same increase in CO<sub>2</sub>). Kimmerer and Kozlowski (1982) found that exposure to O<sub>3</sub> and sulfur dioxide (SO<sub>2</sub>) (and other stresses) could enhance emissions of ethylene, ethane, acetaldehyde, and ethanol from *Pinus resinosa* and *Betula papyrifera* seedlings. Similarly, Chen and Wellburn (1989) found that acidic mist enhanced ethylene emission from *Picea* species. In a recent examination of O<sub>3</sub>-sensitive and -insensitive *Populus* clones, no significant effects of either elevated O<sub>3</sub> or CO<sub>2</sub> on isoprene emission were observed (E. L. Singaas 1998, personal communication), although reductions in isoprene emission seemed to parallel decreases in photosynthesis in O<sub>3</sub>-sensitive clones exposed to elevated O<sub>3</sub>. Turner et al. (1991) and Lerdaun et al. (1997) note that increase in global surface temperatures, regional shifts in precipitation, and biomass/plant species redistribution could result in regional to global increases in NMOC emissions on the order of 25%–50% over 10–100-yr timescales. Regional/global increases in temperature can increase the length of the growing season for temperate and boreal vegetated ecosystems. White et al. (1999), for instance, report that the growing season length of temperate deciduous trees is a linear function of annual mean temperature. A 1° increase in the annual mean temperature is associated with a 5-day increase in length of growing season. They report that the growing season ranges between about 140 days at 6°C and 210 days at 19°C. Although there is a lag in the onset of isoprene production after leaf out, atmospheric warming may lengthen the isoprene emitting season, thereby leading to increases in the net NMOC source. The temperature dependence of both monoterpene and isoprene suggests that emissions will respond favorably to global increases in temperature. Monoterpene emissions will likely increase exponentially with temperature (see Fig. 3) because of the effect of temperature on vapor pressure. Because emissions exhibit Arrhenius temperature kinetics (Guenther et al. 1993), isoprene fluxes will in-

crease in response to warmer environments. Finally, regional to global changes in forest composition resulting from forest management activities, altered fire patterns, and disease impacts can often result in increased NMOC emission potential. This may especially be the case for isoprene emission, which is more common in shade-intolerant, early successional species favored by disturbance and many forest management practices.

### 3. Atmospheric controls on biogenic hydrocarbons fluxes

Once produced within the plant system, molecular and atmospheric transport processes dictate how readily hydrocarbons can be transported from sites of biosynthesis to the atmospheric boundary layer. Thus, this section focuses on the progress made toward identifying and quantifying the atmospheric controls on emissions and transport of hydrocarbons from sites of production to the atmospheric environment.

#### a. Diffusion

Molecular diffusion and atmospheric turbulence are key controls on hydrocarbon transport from sites of biosynthesis to the atmospheric environment. To understand such controls on leaf fluxes it is necessary to consider the mode of production of hydrocarbon compounds. In the case of isoprene, its biosynthesis occurs within chloroplasts (Fall and Wildermuth 1998). Immediately after its formation isoprene diffuses from the chloroplast into the cell cytoplasm matrix, through the cell membranes and eventually travels to the intercellular air space by the process of molecular diffusion. Finally, isoprene diffuses through the stomatal cavity to the boundary layer air above the leaf from which it is transported by turbulent eddies to the overlying atmospheric boundary layer. As described in (1), once produced, at the leaf level, these diffusion processes control the isoprene flux ( $E$ ), which can be quantified by knowing the concentration gradient between the leaf ( $\chi_i$ ) and atmosphere ( $\chi_a$ ) and the total conductance ( $g_T = g_B + g_p$ ) to the isoprene diffusion pathway:

$$E = (\chi_i - \chi_a)(g_B + g_p). \quad (1)$$

The  $g_B$  represents the conductances related to the biological influences on the diffusion process as the isoprene molecules travel from the chloroplast to the

stomatal pores. In the case of gases such as isoprene, due to the large concentration gradient between the leaf interior and atmospheric environment, the  $g_B$  exerts little influence on emissions (Steinbrecher et al. 1997). The  $g_p$  describes the physical processes influencing the gas diffusion from leaf epidermis to the top of the leaf boundary layer. It depends on both the physical characteristic dimensions of foliage, wind speed, and physical properties of isoprene molecules. In contrast to isoprene diffusion, monoterpene molecules travel from the storage structures (i.e., leaf ducts or canals) to the atmosphere. Diffusive conductances driving monoterpene fluxes are the same as those present in isoprene transport, except that monoterpene diffusion process starts from storage sites and thus  $g_B \rightarrow 0$ .

#### b. Measuring hydrocarbon fluxes

Biogenic NMOCs inventories are required to assess the impact of hydrocarbons on regional chemistry. To derive such inventories, several measurement techniques exist to identify chemical species and determine hydrocarbon emissions rates from vegetation. Depending on the scale of measurements, they range from enclosures and environmentally controlled gas exchange systems to measuring hydrocarbon fluxes from individual foliage elements, branches, or even whole plants, to micrometeorological methods to derive emissions at the plant ecosystem level. Below we summarize the theoretical considerations for such measurement approaches, discuss their advantages and disadvantages, and provide relevant sample data on the magnitude of hydrocarbon fluxes from various plant ecosystems.

##### 1) LEAF-BASED FLUXES

Enclosure systems are particularly useful for defining the forcing variables controlling hydrocarbon emissions. Such measurement systems range from whole-plant enclosures (Pir 1995) to controlled-environment cuvette systems (Harley et al. 1996b). Hydrocarbon emission measurements from foliage are made using enclosures such as Tedlar or Teflon bags (Lamb et al. 1987; Steinbrecher et al. 1997) or environmentally controlled gas exchange systems (Fall and Monson 1992; Sharkey and Loretto 1993; Harley et al. 1996?). Several approaches are used to determine hydrocarbon fluxes emitted by foliage. One common approach entails enclosing leaves or branches of known leaf area ( $A$ ) inside cuvettes, and continuously passing atmospheric air through the system at desired flow rates ( $f$ ). As shown in (2), the hydrocarbon emission rate ( $E$ ) is determined by measuring the hydro-

carbon concentration entering ( $\chi_{\text{In}}$ ) and leaving ( $\chi_{\text{Out}}$ ) the cuvette system:

$$E = (\chi_{\text{Out}} - \chi_{\text{In}}) \frac{f}{A}. \quad (2)$$

Foliage remains inside cuvettes for time periods sufficient to gather enough cuvette-air samples for analyses of hydrocarbons. The determination of hydrocarbon concentrations can be achieved using in situ techniques (Hills and Zimmerman 1990). Alternatively, air samples are first gathered in inert canisters or on suitable solid adsorbents for subsequent hydrocarbon analyses using chromatographic methods (Helmig 1999). The data presented in Figs. 3–6 were derived from enclosure systems.

An important consideration in measuring hydrocarbon emissions is the chemical reactions occurring in enclosure systems. For example, Fig. 9 shows the difference in  $\beta$ -caryophyllene emission from orange leaves obtained by enclosing branches of the same tree in cuvettes flushed with ambient air. While substantial emission of  $\beta$ -caryophyllene (a very reactive sesquiterpene) was detected in the cuvette equipped with an  $\text{O}_3$  scrubber, no sesquiterpene emission was measured in the enclosure flushed with air containing atmospheric  $\text{O}_3$  levels (50 ppbv). Since the average residence time of the emission inside the cuvettes was circa 3 min, lifetimes shorter than 2 min were estimated for  $\beta$ -caryophyllene. The lack of measurable fluxes of  $\beta$ -caryophyllene from orange orchards supported the observations made with enclosures and reaction rates determined in the laboratory (see section 4) that sesquiterpenes react faster than measurement timescales.

## 2) CANOPY-LEVEL FLUXES

Enclosure methods are inherently limited because it is difficult to operate chambers for long-term, continuous measurements or to deploy enough replicates to obtain statistically reliable results. Micrometeorological methods enable us to make hydrocarbon fluxes without disturbing the environment of the underlying surface and can be operated during long periods of time. Additionally, these measurements provide spatial averages of hydrocarbon fluxes entering the atmospheric environment. Since it is mainly tree species that release hydrocarbons, most hydrocarbon fluxes reported heretofore pertain to forest ecosystems. The methods applied to determine hydrocarbon fluxes from forest

ecosystems and associated sample datasets are described below.

### (i) Gradient diffusion approach

Many studies have relied on the gradient diffusion method to derive diel and seasonal cycles of NMOC fluxes from several types of forest ecosystems (Lamb et al. 1987; Fuentes et al. 1996; Lamb et al. 1996; Guenther et al. 1996; Ciccioli et al. 1997). In the atmospheric surface layer, it is assumed that a hydrocarbon flux can be characterized by the product of the concentration gradient ( $\partial\chi/\partial z$ ) defined between two levels above the source and an atmospheric eddy diffusivity ( $K_\chi$ ) of the hydrocarbon constituent (3). The  $K_\chi$  can be obtained by invoking the Monin and Obukhov (1954) similarity hypothesis, as shown below:

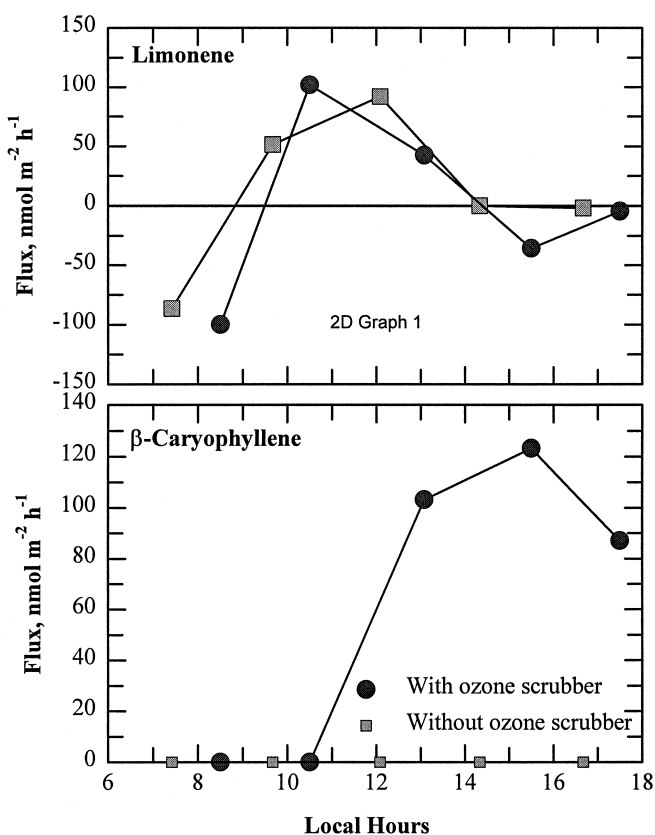


FIG. 9. Emission rates of limonene and  $\beta$ -caryophyllene from orange tree branches measured with two enclosures flushed with ambient air. One was equipped with an ozone scrubber (without ozone) whereas the other received air containing the ambient levels of ozone (50 ppbv) (with ozone). While no effect was detected on limonene, complete removal of  $\beta$ -caryophyllene emission occurred in the cuvette flushed with air containing ozone. Data were collected on 13 June 1997 in Burriana (Valencia, Spain). Measurements were obtained using the cuvette provided by Dr. J. Kesselmeier of the Max Planck Institute (Mainz, Germany). Emission rates are expressed per unit foliage area.

$$F_{\chi} = -K_{\chi} \frac{\partial \chi}{\partial z} = \frac{u_* k (z-d)}{\phi_h} \frac{\partial \chi}{\partial z}, \quad (3)$$

where  $\phi_h$  denotes the diabatic influence function for heat,  $u_*$  signifies the friction velocity (derived from momentum flux ( $\tau$ ) measurements [ $u_* = (\tau/\rho)^{0.5}$ ],  $k$  is the von Kármán constant ( $= 0.4$ ), and  $d$  represents the forest zero plane displacement. The fluxes represent ecosystem emissions and are given by the integrated form of (3) (Fuentes et al. 1996), as shown below:

$$F_{\chi} = \frac{ku_* (\chi_U - \chi_L)}{\ln\left(\frac{z_U - d}{z_L - d}\right) + \psi_{\chi}(\zeta_L) - \psi_{\chi}(\zeta_U)} \quad (4)$$

Above forests  $\zeta$  is taken as  $(z-d)/L$ , where  $L$  is the Monin–Obukhov length ( $L = -u_*^3/[k(g/T_v)H_k]$ ;  $g$  is the gravitational acceleration at the earth's surface,  $T_v$  is the virtual temperature, and  $H_k$  is the virtual kinematic

heat flux). Here,  $\chi_U$  and  $\chi_L$  represent gas concentrations at the upper ( $z_U$ ) and lower ( $z_L$ ) intake levels for air sampling above the surface of interest. The diabatic correction functions (Högström 1988),  $\Psi(\zeta)$ , for  $\chi$  profile are evaluated at  $z_U$  and  $z_L$ . To obtain reliable results, the gas concentration gradients must be determined sufficiently away from the near-field diffusion region above the forest sources (Cellier and Brunet 1992). However, if  $\partial\chi/\partial z$  measurements are taken within the canopy roughness sublayer then an enhancement factor (Cellier and Brunet 1992; Simpson et al. 1998) must be incorporated in the flux calculations. One difficulty of this approach is that the assumption implied in the gradient diffusion approach may be violated due to the uneven distribution of sources in the underlying surface. In a modeling study on the eddy diffusivities for isoprene versus both water vapor and carbon dioxide, Baldocchi et al. (1995) found that the separated source/sink attributes of carbon dioxide do not make its eddy diffusivity a good surrogate for isoprene. Nonetheless, as shown in Fig. 10, this method can capture the main features of diurnal fluxes from vegetated ecosystems.

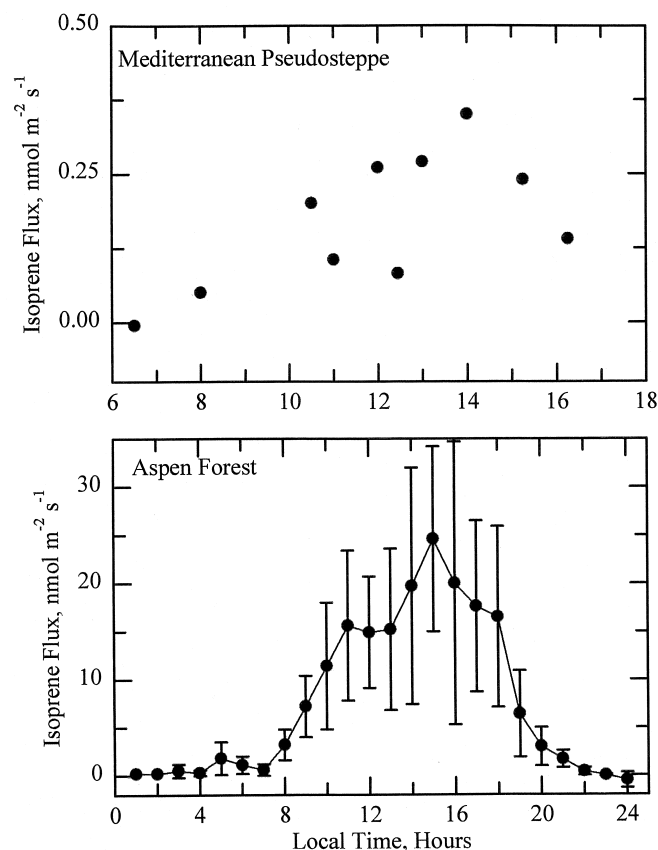


FIG. 10. Isoprene fluxes obtained from Mediterranean pseudosteppe [Ciccioli et al. (1997), filled circles] and aspen forest [Fuentes et al. (1999), filled circles plus STD]. Fluxes are expressed per unit ground area.

#### (ii) Modified Bowen ratio method

The tenet of this approach is that the atmospheric eddy diffusivities are identical for two scalars. Similarity of the diffusivities holds only when the scalar quantities have an identical source/sink distribution within the underlying surface and when gradient measurements are made several turbulent length scales away from sources and sinks. These assumptions allow the calculation of the flux for constituent  $\chi$  ( $F_{\chi}$ ) from measurements of the concentration gradient between two heights ( $\partial\chi/\partial z$ ), combined with the flux ( $F_{\rho}$ ) and gradient ( $\partial\rho/\partial z$ ) measurements of a second constituent  $\rho$ . Thus, it is readily shown that

$$F_{\chi} = F_{\rho} \frac{\partial \chi}{\partial \rho}, \quad (5)$$

where  $\partial\rho$  is measured over the same height interval as  $\partial\chi$ . Traditionally the hydrocarbon fluxes can be obtained by independently measuring  $F_{\rho}$  (e.g., water vapor flux) using in situ techniques such as the eddy covariance approach and its concentration gradient,  $\partial\rho/\partial z$  (Goldstein et al. 1998; Lamanna and Goldstein 1999; Valentini et al. 1997). An uncertainty in this measurement approach is that sources or sinks for constituent  $\rho$  are often not the same as for  $\chi$  because

not all plants release hydrocarbons (Baldocchi et al. 1995). Several workers have applied the modified Bowen ratio to determine hydrocarbon fluxes over various vegetated landscapes. Figure 11 shows strong diurnal variations in the pinene fluxes from a pine–oak forest in Italy.

(iii) *Relaxed eddy accumulation technique*

The relaxed eddy accumulation (REA) approach involves the separation of gas samples into two reservoirs for ascending and descending air. As shown in (6), the flux is related to an empirical coefficient ( $b(\zeta)$ ), the standard deviation of the vertical wind speed ( $\sigma_w$ ), and the difference in the mean hydrocarbon concentration associated with updrafts ( $\chi_u$ ) and downdrafts [ $\chi_d$ , Businger and Oncley (1990)]:

$$F_\chi = b(\zeta)\sigma_w(\chi_u - \chi_d). \quad (6)$$

The empirical coefficient  $b(\zeta)$  weakly depends on atmospheric stability (Businger and Oncley 1990). However, simulations using wind, humidity, and temperature indicate that  $b(\zeta)$  has the value of  $0.6 \pm 0.06\%$  (Businger and Oncley 1990; Pattey et al. 1993). The vertical wind speed provided by sonic anemometers is used to divert air to reservoirs associated with updrafts and downdrafts and, thus, gathering air to determine  $\chi_u$  and  $\chi_d$ . Instead of using reservoirs to store air samples, Ciccioli et al. (1997) demonstrated the value of an adsorbent cartridge REA method for measuring NMOC fluxes over an orange orchard. The REA system relies upon fast solenoid valves to switch and direct air into updraft and downdraft reservoirs depending on the vertical wind speed ( $w$ ) measured by sonic anemometers. It is common to conduct conditional sampling depending upon a vertical wind speed threshold value, typically vertical wind speeds exceeding 50%–75% of  $\sigma_w$  or when  $w > 0.05 \text{ m s}^{-1}$  (Valentini et al. 1997; Pattey et al. 1993; Bowling et al. 1999). Although the REA approach is straightforward to apply, the method is too labor intensive and may include large uncertainties in the fluxes determined for tall forests. In particular, errors may be associated with fluxes due to the lack of real-time coordinate rotation of the wind components and separation of airstreams into ascending and descending air samples. When compared with flux-gradient measurements, REA fluxes agree within 20%, the latter approach yielding larger fluxes (Guenther et al. 1996; Bowling et al. 1998). For isoprene over a black spruce forest, Pattey et al. (1999) found that modified Bowen ratio method yielded significantly lower fluxes com-

pared to the REA approach. Figure 12 shows an example of strong diurnal REA isoprene fluxes measured above a hickory–oak forest in Oak Ridge, Tennessee.

(iv) *Eddy covariance approach*

This approach is based upon the Reynold’s averaged turbulent flux terms in which the flux of a scalar ( $\chi$ ) such as isoprene leaving a forested surface can be derived from the covariance between  $w$  and  $\chi$  as shown below:

$$F_\chi = \overline{w\chi} = \overline{(\bar{w} + w')(\bar{\chi} + \chi')} = \overline{w'\chi'}, \quad (7)$$

where  $w'$  and  $\chi'$  are the deviation components of  $w$  and  $\chi$ , respectively, from the mean quantities. The eddy covariance method is considered a more rigorous approach for measuring fluxes and has been widely applied to determine carbon dioxide, water vapor, and heat fluxes to or from forests. For biogenic hydrocarbon flux measurements, the application of the eddy covariance approach is restricted by the lack of suitably fast chemical sensors. The single exception is the isoprene analyzer developed by Hills and Zimmerman (1990), and recently employed by Guenther and Hills (1998) to measure isoprene fluxes over a mixed forest (North Carolina) dominated by oak trees where isoprene fluxes ranged from near zero ( $0.01 \pm 0.03 \text{ mg C m}^{-2} \text{ h}^{-1}$ ) at nighttime to  $14 \text{ mg C m}^{-2} \text{ h}^{-1}$  at midday during the middle of the growing season. In this application, air is sampled through an inlet collocated with a three-dimensional sonic anemometer and drawn through tubing to the

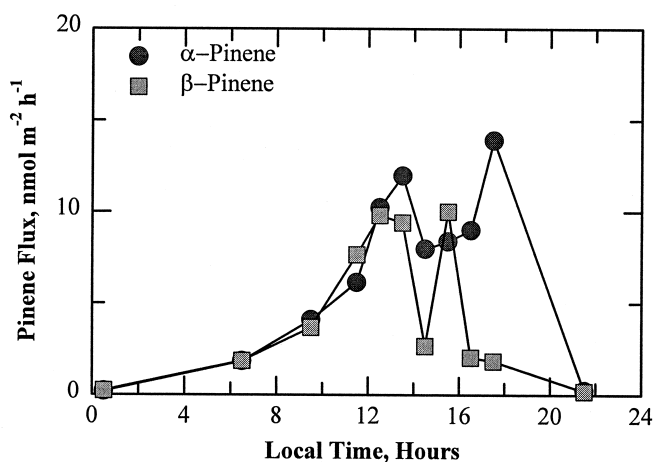


FIG. 11. Pinene fluxes obtained from a pine–oak forest in Italy using the modified Bowen ratio approach (Valentini et al. 1997). Fluxes are expressed per unit ground area.

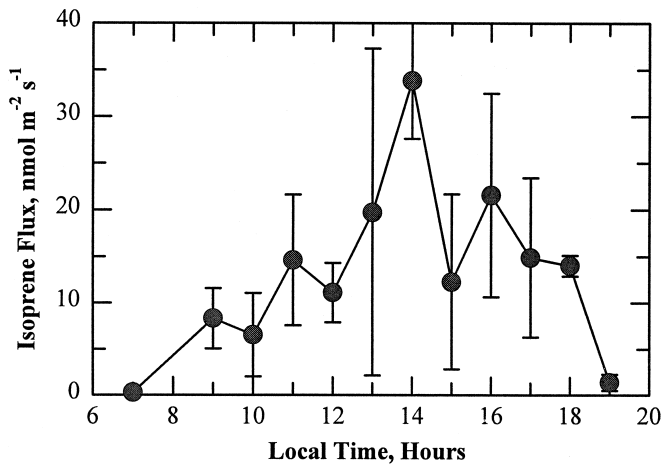


FIG. 12. Isoprene fluxes obtained from an oak-hickory forest in Oak Ridge, TN, using the relaxed eddy accumulation (adapted from Lamb et al. 1996). Fluxes are expressed per unit ground area.

analyzer located either on a tower or at ground level. In processing the results, it is necessary to perform a coordinate rotation on the measured wind components, account for the lag time of sample flow from air sampling inlet to detector, correct for the influence of density fluctuations upon the measured isoprene flux (Webb et al. 1980), and consider the loss of flux due to damping of high-frequency eddy motions within the sampling tubing. Typical results from the application of this method are shown in Fig. 13 for two weeks of measurements obtained at an aspen-maple deciduous forest in northern Michigan. In this case, the time series of isoprene flux has been normalized to the maximum measured flux. The results show strong diurnal cycles of isoprene emissions and also exhibit relatively large day to day variability. In the first part of the period (days 213–216), air masses were warm, skies were clear, and maximum isoprene fluxes exceeded 0.8 (normalized). Cloudy and rainy conditions prevailed in the middle of the period (days 218–220), and the peak normalized emissions decreased to less than 0.4. Near the end of the period, conditions remained cool, but skies were clear, and the peak normalized emissions reached approximately 0.5. The primary advantage of the eddy flux method is the availability of continuous measurements, which can be maintained for extended periods of time. The disadvantages involve the need for a suitably fast chemical sensor, and the

development and maintenance of instrumentation and software systems needed to apply the method. In the case of existing isoprene analyzers, Guenther and Hills (1998) established that interferences from other compounds (e.g., propene, ethene, methyl-butenol, methacrolein, and methyl vinyl ketone) over most North American landscapes can be approximately 5% of the total flux.

### 3) LANDSCAPE-LEVEL FLUXES

The main goal of deriving hydrocarbon fluxes is to provide emissions for regions. Thus, hydrocarbon concentration measurements at several altitudes using tethered balloon systems provide contextual information to derive hydrocarbon fluxes canvassing spatial scales extending from the canopy top to well into the convective boundary layer. The mass balance approach provides the basis to derive hydrocarbon fluxes at the landscape level. As noted in (8), if the mean horizontal flow ( $u$ ) is aligned with the west-to-east axis ( $x$ ) this method requires knowledge of spatial ( $\partial\chi/\partial x$ ) and vertical ( $\partial\chi/\partial z$ ) changes in hydrocarbon concentrations, and flux changes ( $\partial F_\chi/\partial z$ ) within the atmospheric mixed layer to obtain hydrocarbon fluxes (Guenther et al. 1996; Zimmerman et al. 1988):

$$\frac{\partial\chi}{\partial t} + u(z)\frac{\partial\chi}{\partial x} + w(z)\frac{\partial\chi}{\partial z} = -\frac{\partial F_\chi}{\partial z} + Q_\chi, \quad (8)$$

where  $Q_\chi$  is the source or sink of hydrocarbon within the atmospheric mixed layer and  $w(z)$  is the vertical velocity field defined at altitude  $z$ . Several simplifying

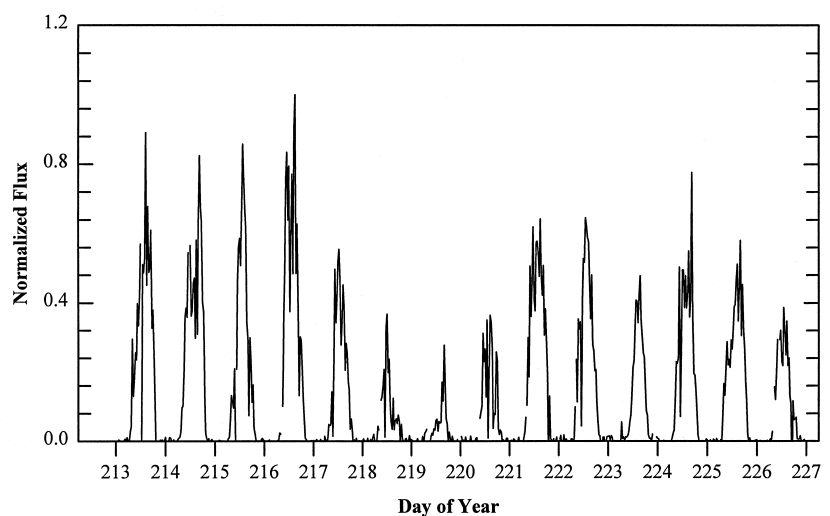


FIG. 13. Eddy covariance isoprene fluxes from an aspen forest (MI) during Aug 1998.

ing assumptions can be made in (8) to derive hydrocarbon fluxes ( $F_{\chi^0}$ ) from a given surface. For example, assuming a well-mixed atmospheric layer ( $\partial\chi/\partial z = 0$ ), integrating (8) from the surface to the top of the convective layer ( $z_*$ ), and solving for  $F_{\chi^0}$ , the following relationship is obtained:

$$F_{\chi^0} = z_* \frac{\partial \bar{\chi}}{\partial t} + z_* \bar{u} \frac{\partial \bar{\chi}}{\partial x} + F_{\chi z_*} - z_* Q_{\chi}. \quad (9)$$

The overbars on  $\chi$  and  $u$  denote vertical averages from the surface to  $z_*$ . The hydrocarbon flux at  $z_*$  ( $F_{\chi z_*}$ ) is derived in terms of surface-based measurements (Guenther et al. 1996). For hydrocarbons such as isoprene the term  $Q_{\chi}$  during the daytime can be determined from the combined reaction of  $O_3$  and OH with isoprene (Guenther et al. 1996). Additionally, the  $z_*$  needs to be known either from tethered balloon measurements or modeling systems. The fidelity of results obtained from this approach depends on the characteristics and spatial extent of the underlying surface. Several studies (Greenberg et al. 1999; Guenther et al. 1996; Isebrands et al. 1999; Helmig et al. 1998; Zimmerman et al. 1988) have employed this approach to derive landscape-level isoprene fluxes. For example, in western Washington the mixed layer flux method was applied to derive landscape-level isoprene fluxes from concentration profiles obtained from tethered balloons (Fig. 14). In this case, the landscape is dominated by conifer species sparsely interspersed with aspen. As a result, the effective isoprene flux is relatively small. Nonetheless, a linear relationship exists when estimated isoprene fluxes and product of light and temperature correction coefficients [see Eq. (10) below] are correlated. Such linear correlation yields landscape-level isoprene emission rates, which in the case of the data for Fig. 14 gives  $38.3 \mu\text{molC m}^{-2} \text{h}^{-1}$  defined at a temperature of  $30^\circ\text{C}$  and photosynthetically active radiation (PAR) of  $1000 \mu\text{mol}^{-2} \text{m}^{-1} \text{s}$ . This approach (Fig. 14) is useful for estimating landscape emission fluxes normalized to standard conditions and provides a basis for evaluating regional hydrocarbon inventories derived with modeling systems described in section 3c. For the latter, tethered balloon flux estimates and model calculations range from good agreement [for northern hardwood forests; Isebrands et al. (1999)] to discrepancies within a factor of 2 (Greenberg et al. 1999).

Only selected regional fluxes of hydrocarbons have been measured from aircraft using the REA or eddy covariance approach. Recently, using the REA ap-

proach, Zhu et al. (1999) reported aircraft-based isoprene fluxes for boreal aspen and black spruce forests. In addition to providing a means to verify the fidelity of inventory modeling systems, aircraft-based fluxes can be used to verify tower-based fluxes.

Before leaving this section, the reader should be aware that establishing reliable NMOC fluxes is a formidable task. The principal difficulty stems from the interrelationship between horizontal flux “footprints” detected by flux measurement systems and the distribution of hydrocarbon emitting biomass. Because not all plant species release hydrocarbons, the source footprint for hydrocarbons may not coincide with that for scalars such as water vapor or carbon dioxide. Therefore, hydrocarbon flux measurements need to be interpreted with detailed biomass surveys and biomass data must be linked with source footprint calculations (Lamb et al. 1996). When such data integration is introduced at the single plant canopy level, comparisons between model and measurement results for heterogeneous sources agree within 50% (Balducchi et al. 1999).

### c. Modeling hydrocarbon emissions

To study the impacts of biogenic hydrocarbons on regional and global chemistry, hydrocarbon emissions need to be determined. This task first requires the development or use of emission algorithms at the leaf level. Then the integration of leaf-based emissions to the landscape dimension is achieved by knowing both the distribution of active biomass and environmental factors influencing hydrocarbon emissions. In the case of isoprene, foliage emission rates ( $E_{\text{isoprene}}$ ) are estimated

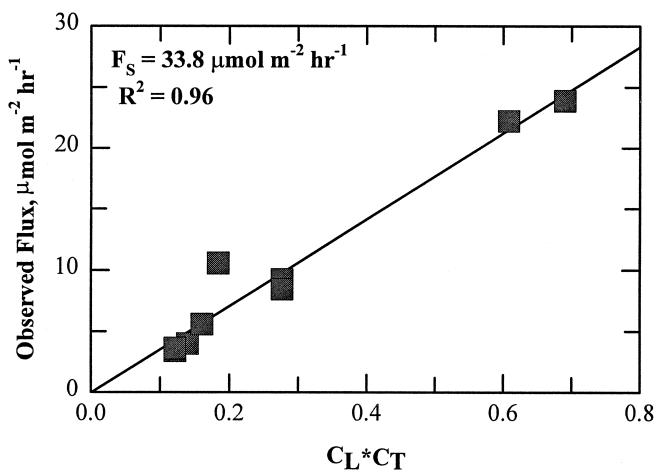


FIG. 14. Landscape-based, mixed layer isoprene flux estimates from tethered balloon measurements vs the product of the light and temperature correction algorithms for a site in the western part of WA during Aug 1996 (from Lamb et al. 1997). Fluxes are expressed per unit ground area.

using an emission factor ( $E_s$ ), which is modulated by both intercepted PAR [ $f(\text{PAR})$ ] and foliage temperature [ $f(T_L)$ ], as shown below (Guenther et al. 1993):

$$E_{\text{Isoprene}} = E_s[f(\text{PAR})][f(T_L)], \quad (10)$$

where  $E_s$  is plant-species specific and normalized at a specified leaf temperature ( $T_L$ ) and intercepted PAR. The modulating functions,  $f(\text{PAR})$  and  $f(T_L)$ , are nondimensional and adjust the emission rate according to variations of leaf temperature and intercepted PAR. The  $f(\text{PAR})$  assumes a value of 1.0 at  $\text{PAR} = 1000 \mu\text{mol m}^{-2} \text{s}^{-1}$ . The  $f(T_L)$  defines the temperature dependency of enzymatic activity responsible for isoprene emissions. It takes the value of 1.0 at temperature  $T_s$  (303 K) (Guenther et al. 1993). Figure 4 shows isoprene emissions as predicted by  $f(T_L)$  whereas Fig. 5 includes fluxes as estimated with  $f(\text{PAR})$ .

In contrast to isoprene, the environmental variable controlling monoterpene emissions is foliage temperature ( $T_L$ ), which dictates the vapor pressure of monoterpenes in leaves. Thus, the relationship between instantaneous monoterpene emissions ( $E_{\text{Mono}}$ ) and temperature is described below (Tingey 1981; Guenther et al. 1993):

$$E_{\text{Mono}} = E_s \exp[\beta(T_L - T_s)], \quad (11)$$

where  $E_s$  is the monoterpene emission rate at a nominal temperature  $T_s$  ( $= 303 \text{ K}$ ) and  $\beta$  is an empirical coefficient derived from measurements. Based on measurements from several plant species the  $\beta$  values range from 0.06 to 0.14 per K, but most modeling studies include the average value of 0.09 per K (Guenther et al. 1993). Figure 3 illustrates monoterpene emissions versus foliage temperature. The question whether sesquiterpene emissions can be described by temperature-dependent or light- and temperature-dependent algorithms is still unresolved due to insufficient emission measurements. It is likely that plants having storage compartments will emit sesquiterpenes following the algorithm outlined by Eq. (11).

Environmental variables must be known spatially and temporarily to determine hydrocarbon emissions from vegetated ecosystems. Both foliage temperature and light regimes vary with plant canopy depth. To estimate the amount of light intercepted by foliage inside plant canopies, several approaches are often adopted. The simplest method involves exponential decay functions in which PAR is estimated [at several levels ( $z$ ) within the plant canopy] as a function

of above-canopy PAR [ $\text{PAR}(h_c)$ ;  $h_c$  is the canopy height], cumulative leaf area index ( $L(z)$ ), and sine of the solar elevation angle ( $\phi$ ) (Geron et al. 1994):

$$\text{PAR}(z) = \text{PAR}(h_c) \exp\left(-\frac{\delta L(z)}{\sin \phi}\right). \quad (12)$$

The PAR extinction coefficients ( $\delta$ ) employed in these relationships are either derived through measurements or adopted from reported values ( $0.20 \leq \delta \leq 0.85$ ).

A second radiative transfer approach entails probability theory to describe photon transmission throughout plant canopies (Baldochi et al. 1999; Gutschick 1991; Myneni et al. 1989). In this approach light distribution inside clumped plant canopies is determined based on the beam probability penetration function (Gutschick 1991),  $P$ , as shown below:

$$P = \exp\left(-\frac{L(z)G\Omega}{\sin \phi}\right), \quad (13)$$

where  $G$  is the leaf orientation function and represents the relative projection area of leaf elements in the direction of the solar beam and  $\Omega$  is the canopy clumping factor whose value for most natural forests is  $0 \leq \Omega \leq 1$ . The probability of diffuse radiation is computed by integrating (13) over the hemisphere of the sky. Light scattering is calculated following the methods suggested by Norman (1979).

A third approach involves the radiation propagation equation (Dickenson 1983; Sellers 1985). In this method, the plant canopy is treated as an active medium in partitioning the incoming radiation stream into intercepted, reflected, transmitted, and absorbed components. Such processes are incorporated in the radiation propagation equation (Dickenson 1983):

$$\begin{cases} -\mu \frac{dF \uparrow}{dL} + [1 - (1 - \beta)\omega]F \uparrow - \omega\beta F \downarrow = \omega \bar{\mu} K \beta_0 e^{(-KL)}, \\ \mu \frac{dF \downarrow}{dL} + [1 - (1 - \beta)\omega]F \downarrow - \omega\beta F \uparrow = \omega \bar{\mu} K (1 - \beta_0) e^{(-KL)}, \end{cases} \quad (14)$$

where  $F \uparrow$  and  $F \downarrow$  represent the upward and downward diffuse radiative fluxes, respectively, normalized to the incident PAR measured above the forest;  $K$  is the light extinction coefficient;  $\omega$  denotes the PAR leaf scattering coefficient and equals the sum of the leaf reflec-



tion ( $\alpha$ ) and transmission ( $\Psi$ ) coefficients;  $L$  is the downward cumulative leaf area index;  $\mu$  is the average inverse diffuse optical depth per unit leaf area; and  $\beta$  and  $\beta_0$  are the upscatter parameters for the diffuse and direct beam, respectively. Sellers (1985) provided the mathematical solution to (14) and Fuentes et al. (1999) incorporated (14) to determine isoprene emissions from an aspen forest.

A more complete description of the radiative transfer inside the plant canopy is provided by the photon transport equation (Ross 1981). In this approach, the radiation field inside the canopy is decomposed into the following parts: unscattered direct beam specific energy intensity  $i_r^0(L, \Omega)$  ( $\mu\text{mol photon m}^{-2} \text{sr}^{-1} \text{s}^{-1}$ ), unscattered diffuse skylight specific energy intensity  $i_f^0(L, \Omega)$ , direct beam-originated scattered specific energy intensity  $i_r^s(L, \Omega)$ , and diffuse skylight-originated scattered specific energy intensity  $i_f^s(L, \Omega)$ . Here,  $\Omega$  denotes a direct defined by  $(\theta, \phi)$ , where  $\theta$  is the polar zenith angle and  $\phi$  is the azimuth angle. The unscattered intensities are given by

$$i_r^0 = \delta(\Omega - \Omega_0) \frac{\text{PAR}_r}{-\mu_0} \exp\left(\frac{G(\mu_0)}{\mu_0} L\right) \quad (15)$$

and

$$i_f^0(L, \Omega) = \frac{\text{PAR}_f}{\pi} \exp\left(\frac{G(\mu)}{\mu} L\right), \quad (16)$$

where  $\mu_0 = -\sin\beta_0$  (note  $\mu_0$  differs from  $\mu_0$  by sign). The functions  $i_r^s(L, \Omega)$  and  $i_f^s(L, \Omega)$  are obtained by solving the following photon transport equation (Ross 1981; Myneni et al. 1989):

$$-\mu \frac{\partial(L, \Omega)}{\partial L} + G(\Omega)i(L, \Omega) = \frac{1}{\pi} \int_{4\pi} d\Omega' \Gamma(\Omega' \rightarrow \Omega) i(L, \Omega') \quad (17)$$

where  $\mu$  is the cosine of the polar angle  $\theta$  with “-” for the descending direction relative to a horizontal plane and  $\Gamma(\Omega' \rightarrow \Omega)$  is the area scattering phase function from the direction  $\Omega'$  to  $\Omega$ . The area scattering phase function  $\Gamma(\Omega' \rightarrow \Omega)$  depends on both the leaf normal orientation distribution and the leaf optical characteristics. It is expressed as (Ross 1981; Myneni et al. 1989)

$$\frac{1}{\pi} \Gamma(\Omega' \rightarrow \Omega) = \frac{1}{2\pi} \int_{2\pi} g(\Omega_L) |\Omega_L \Omega'| f(\Omega' \rightarrow \Omega, \Omega_L) d\Omega_L, \quad (18)$$

where  $f(\Omega' \rightarrow \Omega, \Omega_L)$  is the leaf scattering transfer function for which the bi-Lambertian leaf scattering model is used (Myneni et al. 1989):

$$f(\Omega' \rightarrow \Omega, \Omega_L) = \begin{cases} \frac{r_L |\Omega_L \Omega|}{\pi}, (\Omega_L \Omega)(\Omega_L \Omega') \\ \frac{t_L |\Omega_L \Omega|}{\pi}, (\Omega_L \Omega)(\Omega_L \Omega') \end{cases}, \quad (19)$$

where  $r_L$  and  $t_L$  are the leaf reflection and transmission coefficients, respectively. The photon transport equation (19) is solved by the method of successive orders of scattering approximations whose descriptions can be found in Myneni et al. (1989).

Given that hydrocarbon emissions differ markedly among shaded and sunlit leaves (Harley et al. 1996b, 1997; Fig. 5), it is critical to divide the canopy foliage into sunlit and shaded fractions. For plant canopies with a random leaf area distribution, the sunlit fraction of  $L$  can be determined as shown below (Fuentes et al. 1996; Guenther et al. 1995):

$$F_{\text{Sun}} = \frac{\sin \phi}{0.5L} \left( 1 - \exp\left[-\frac{0.5L(z)}{\sin \phi}\right] \right). \quad (20)$$

The shaded fraction of  $L$  is determined from subtraction. If models do not consider the partitioning between sunlit and shaded leaves, isoprene emissions can be overestimated (Geron et al. 1997; Huber et al. 1999). Using the approaches described above [Eq. (19)], Fig. 15 shows an example of 20% overestimates of isoprene emissions without the partitioning of shaded and sunlit foliage. During a clear day, the noontime isoprene flux tends to be overestimated if sunlit and sunshaded leaves are not separated. This is because the process of averaging PAR received by sunlit and shaded leaves reduces the saturation effect of high PAR on isoprene emission by sunlit leaves and thus overestimates the contribution from these leaves to canopy fluxes. During the early morning or late afternoon, however, the fraction of sunlit leaves is much smaller and the fraction of diffuse radiation, which

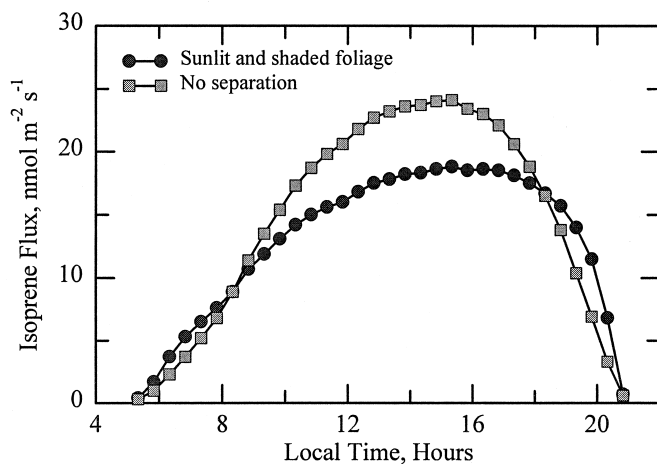


FIG. 15. Modeled isoprene emissions from an aspen forest utilizing radiative transfer methods without (filled squares) and with (filled circles) partitioning of sunlit and shaded leaves.

transfers deeper into plant canopies than the direct beam radiation and thus has a bigger efficiency for isoprene emission, is much bigger than at noontime. Because the no-separation scheme ignores the differences between diffuse and direct radiative transfer in plant canopies, it underestimates the contribution from the diffuse radiation to canopy fluxes during early morning and late afternoon, and leads to underestimation of canopy fluxes.

Foliage temperature is calculated throughout plant canopies to determine enzymatic rates associated with isoprene emissions or volatilization of monoterpenes. To determine foliage temperature inside plant canopies several approaches have been applied. One involves the assumption that the air temperature above the plant canopy is the same as foliage temperature. In this approach foliage temperature is invariant with canopy depth (Geron et al. 1994; Pierce et al. 1998). Depending on plant canopy structure this method can introduce uncertainties of as much as 2°–8°C during the daytime (in the upper canopy), the foliage temperature being underestimated. Such underestimates in foliage temperature can translate in reduced hydrocarbon emissions that may be lower than 50% when compared to measurements (Lamb et al. 1996).

Another method treats plant canopies as layers and for each layer the complete energy balance is determined to yield foliage temperature. Utilizing measurements taken above the plant canopy as model input, the energy balance for each layer is determined based on light absorption, foliage radiative and convective heat fluxes, and leaf latent heat flux. Such fluxes are computed utilizing turbulent transport theory and the radiative transfer models described above (Baldochi

et al. 1999; Huber et al. 1999; Lamb et al. 1996). To gauge the fidelity of these modeling systems, here we report modeled and measured temperature in upper and lower regions of a 22-m mixed deciduous forest (Fig. 16). In the upper regions of canopies, predicted temperatures for sunlit leaves can yield foliage temperatures 7°C warmer than air temperature while shaded leaves can be 2°C warmer than air temperature (Fig. 16). Measurements averaged over many leaves in the upper canopy can be 1°–3°C warmer than air temperature. In the lower canopy, the predicted sunlit temperature can be 3°C warmer than air temperature while calculated shaded leaf temperatures can be 1°C cooler than air temperature. The latter closely matches measurements averaged over several leaves in the lower canopy (Fig. 16).

The emission algorithms presented above [Eqs. (10) and (11)] require a priori knowledge of  $E_s$  values to derive hydrocarbon fluxes. Because leaves undergo physiological and development changes over the course of the growing season the  $E_s$  values vary accordingly. As noted in section 2, experimental data reported to date indicate that  $E_s$  values change considerably with plant species (Isidorov 1994; Guenther et al. 1994; Monson et al. 1994), ranging from no fluxes among herbaceous plants to large emissions (~100 nmol m<sup>-2</sup> s<sup>-1</sup>) among the *Quercus* genera. Additional factors influencing  $E_s$  include nutrient status (Litvak et al. 1996), soil moisture content (Sharkey and Loreto 1993; Fang et al. 1996), and foliage developmental stage (Grinspoon et al. 1991; Monson et al. 1994; Fuentes et al. 1995). To construct reliable modeling systems to derive hydrocarbon inventories, all controls over hydrocarbon emissions need to be incorporated. To characterize the seasonal variations of isoprene emissions, Monson et al. (1995) and Fuentes and Wang (1999) defined  $E_s$  in terms of thermal degree units. These are only limited datasets from selected plant species and more seasonal hydrocarbon fluxes for coniferous and other deciduous forest ecosystems are required.

To derive hydrocarbon emissions at the forest and regional levels, the distribution of active biomass must be known in both time and space. At the single canopy level, plant distribution and species composition are established through forest inventory surveys. Also, because the amount of foliage changes with season, the biomass foliage is determined by measuring the temporal distribution of leaf area using inferential methods that are verified with measurements of leaf area from leaf litter fall (Fuentes et al. 1999). Such data

can be related to specific leaf weight and thus derive biomass densities for single forest ecosystems. The vertical leaf area distribution is rather difficult to define. However, by taking spherical photographs at several levels within the canopy it is possible to determine the vertical leaf area distribution in most deciduous forests. At the regional scale plant distribution and species composition are derived from forest inventory surveys (Geron et al. 1994) or satellite information (Guenther et al. 1995). For the model domain, foliar density is derived from vegetation classes to reflect several categories of hydrocarbon emissions. Within a given landscape, biomass density can vary with season and from year to year. To account for such biomass changes, several empirical relationships have been derived utilizing satellite normalized difference vegetation indexes (Geron et al. 1994; Guenther et al. 1995).

Finally, specific leaf weight is also adjusted with canopy depth to account for the effect that upper-canopy leaves are heavier than the ones in the bottom of the forest canopy. In the case of isoprene, emission rates scale with photosynthetic capacity (not so during the leaf-out period). Both vary with specific leaf weight (Harley et al. 1997) and leaf nitrogen (Monson et al. 1994; Litvak et al. 1996). To accommodate such relationships, the  $E_s$  values are adjusted with depth in the canopy according to exponential functions of leaf area index. The combined effect of these adjustments is to reduce emissions by 30%–50% of that predicted without accounting for the vertical specific weight reduction downward through the forest canopy (Geron et al. 1994). On a diurnal basis, multilayered models have been evaluated to determine isoprene emissions from homogeneous and heterogeneous forests (e.g., Baldocchi et al. 1999; Huber et al. 1999; Lamb et al. 1996). When information on the spatial distribution of biomass and isoprene source footprint are included, models produce isoprene emissions that compare within 50% of measurements (Fig. 17).

As an example of the isoprene emission potential, Fig. 18 shows large spatial changes in emission rates for North America. The emissions represent predicted July average emissions as function of both variations in cli-

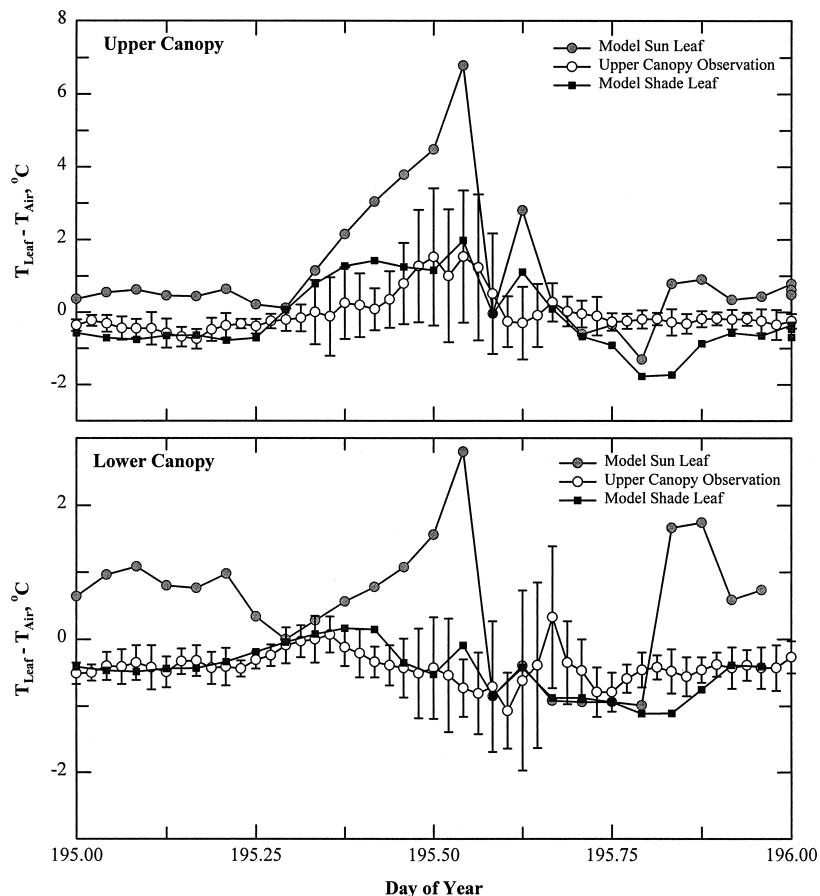


FIG. 16. Comparison of measured and predicted leaf temperatures in a mixed deciduous forest. Measured temperatures and predicted temperatures are from a numerical canopy model (Harley and Baldocchi 1995).

mate and land cover. Emission rates range from less than  $0.1 \text{ nmol m}^{-2} \text{ s}^{-1}$  from grassland and agricultural landscapes to over  $10 \text{ nmol m}^{-2} \text{ s}^{-1}$  from forest landscapes with a high proportion of isoprene emitting

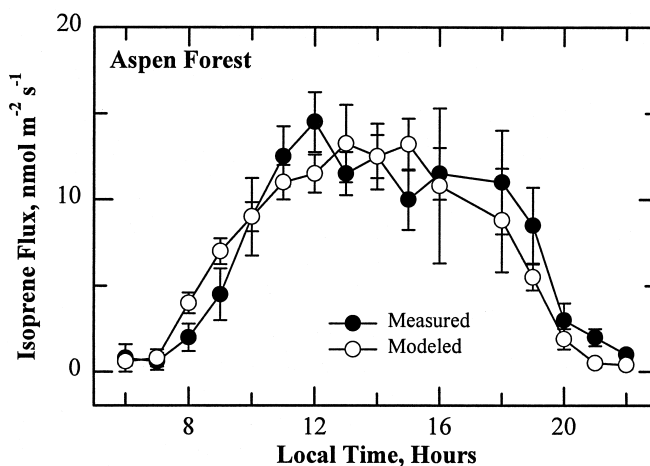


FIG. 17. A comparison between measured and calculated flux densities of isoprene over an aspen forest (data from Baldocchi et al. 1999). Fluxes are expressed per unit ground area.

trees. The shown latitudinal changes in emissions result largely because of the distribution of isoprene active biomass.

Recently, Guenther et al. (1999) derived biogenic hydrocarbon emissions on an annual basis for all of North America. This inventory is summarized in Fig. 19 in terms of the hydrocarbon class emission totals weighted by the reactivity with OH radical. On this basis, in North America biogenic hydrocarbons are dominated by isoprene (51%), terpenes (31%), and oxygenated NMOC (16%) species. Together these three groups account for 98% of all the biogenic hydrocarbon emissions. Thus, in terms of the role of biogenic NMOCs in photochemistry, it seems clear that efforts to improve emission models for isoprene, terpenes, and oxygenated NMOCs should receive a high priority in terms of future research.

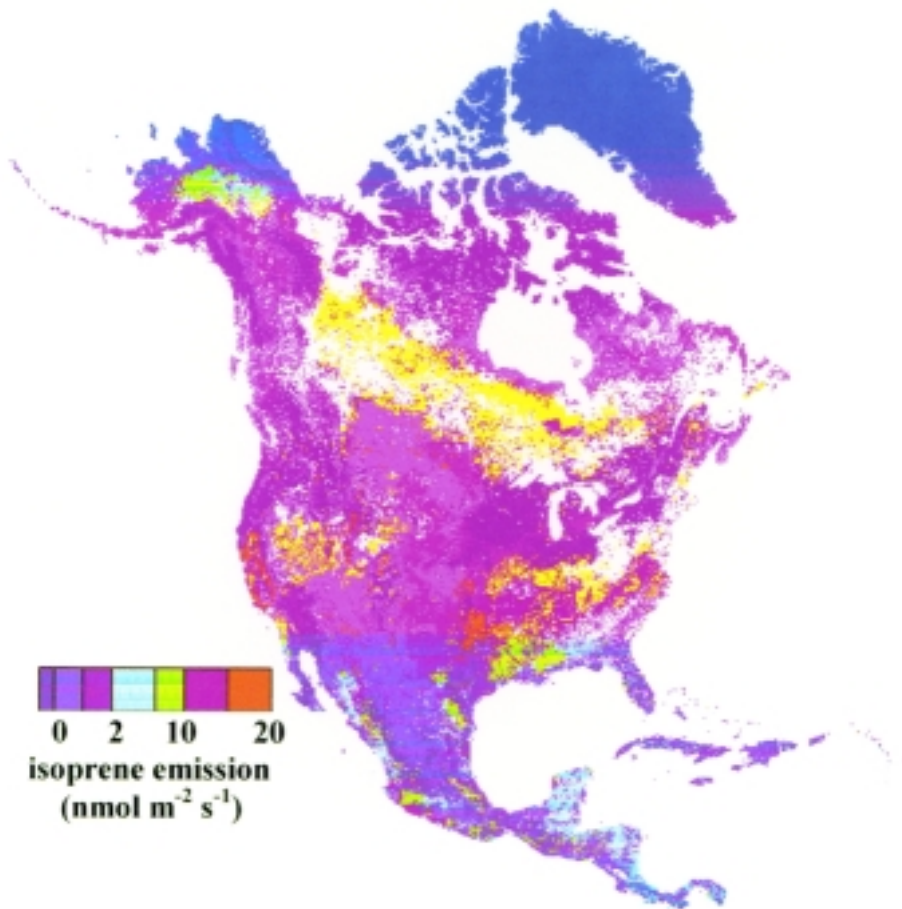


FIG. 18. The spatial distribution of predicted Jul average isoprene emissions for North and Central America. Emission rates are expressed per unit ground area.

#### 4. Chemistry of phytogenic volatile organic compounds

As is the case for other volatile organic compounds in the atmosphere, biogenic NMOC can be removed from the atmosphere by the physical processes of wet deposition and dry deposition, and are transformed in the atmosphere by photolysis, reaction with the hydroxyl (OH) radical, reaction with the nitrate ( $\text{NO}_3$ ) radical, reaction with  $\text{O}_3$  and/or, in certain times and places, reaction with the chlorine (Cl) atom (Jobson et al. 1994; Nordmeyer et al. 1997; Atkinson and Arey 1998). The absolute and relative importance of these removal and transformation processes, and hence the overall tropospheric lifetimes, depend on the specific chemical, although generalizations can be made based on the chemical and structural characteristics of the biogenic NMOC. For most biogenic NMOCs, dry and wet depositions are expected to be of minor importance, but may contribute to the tropospheric removal of those NMOCs that have a low Henry's law

constant and are chemically long lived (examples being methanol and possibly such atmospheric reaction products as hydroxynitrates and hydroxycarbonyls).

In the stratosphere, molecular oxygen and  $\text{O}_3$  absorb solar radiation below  $\sim 290$  nm, and hence only radiation of wavelengths  $> 290$  nm ("actinic" radiation) present in the troposphere can lead to photolysis of biogenic NMOCs. Of the biogenic NMOCs that have been studied to date, only aldehydes and ketones (Hallquist et al. 1997; Atkinson and Arey 1998) absorb actinic radiation. Photolysis is an important tropospheric loss process for acetone (Gierczak et al. 1998) and may also be important for biogenic NMOC reaction products such as organic nitrates and carbonyl-containing compounds (Hallquist et al. 1997; Atkinson et al. 1999). The processes leading to the presence of  $\text{O}_3$ , OH radicals, and  $\text{NO}_3$  radicals in the troposphere are briefly discussed below.

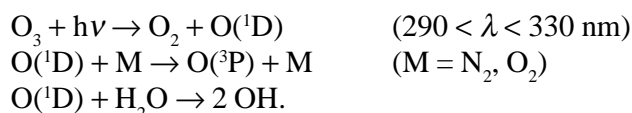
##### a. Tropospheric ozone

Ozone is transported downward by eddy diffusion from the stratosphere into the troposphere (Roelofs

and Lelieveld 1997) and also is formed photochemically in situ in the troposphere from the interactions of volatile organic compounds (including biogenic NMOCs) and oxides of nitrogen ( $\text{NO} + \text{NO}_2 = \text{NO}_x$ ) in the presence of sunlight (Roelofs and Lelieveld 1997). These sources of tropospheric  $\text{O}_3$  are balanced by in situ photochemical destruction and by dry deposition at the earth's surface (Roelofs and Lelieveld 1997), resulting in the presence of  $\text{O}_3$  throughout the troposphere with mixing ratios at "clean" ground level sites of 10–40 parts per billion (ppb) (Logan 1985; Oltmans and Levy 1994). In polluted air masses on urban and regional scales,  $\text{O}_3$  mixing ratios can exceed 100 ppb.

*b. Hydroxyl radicals in the troposphere*

Photolysis of  $\text{O}_3$  present in the troposphere at wavelengths  $> 290$  nm leads, in part, to the formation of the electronically excited oxygen atom,  $\text{O}(^1\text{D})$ , which is seen either deactivated to ground-state oxygen,  $\text{O}(^3\text{P})$  atoms, or reacts with water vapor to generate OH radicals (Atkinson et al. 1997):



The photolysis of  $\text{O}_3$  results in the formation of OH radicals only during daylight hours, and OH radical concentrations therefore exhibit a pronounced diurnal profile with the concentration peaking at around solar noon for clear-sky conditions (Tanner et al. 1997). Peak daytime OH radical concentrations are  $\sim(2\text{--}10) \times 10^6$  molecule  $\text{cm}^{-3}$  for measurements carried out at midlatitude Northern Hemisphere sites (Brauers et al. 1996; Mount et al. 1997; Tanner et al. 1997). A diurnally, seasonally, and annually averaged global tropospheric OH radical concentration of  $1.0 \times 10^6$  molecule  $\text{cm}^{-3}$  (24-h average) has been estimated from the emissions, atmospheric concentrations, and atmospheric chemistry of methyl chloroform (Prinn et al. 1995; Hein et al. 1997).

In polluted air masses OH radicals are also formed during daylight hours from the photolysis of nitrous

**Abundance (%) of biogenic NMOCs by class**

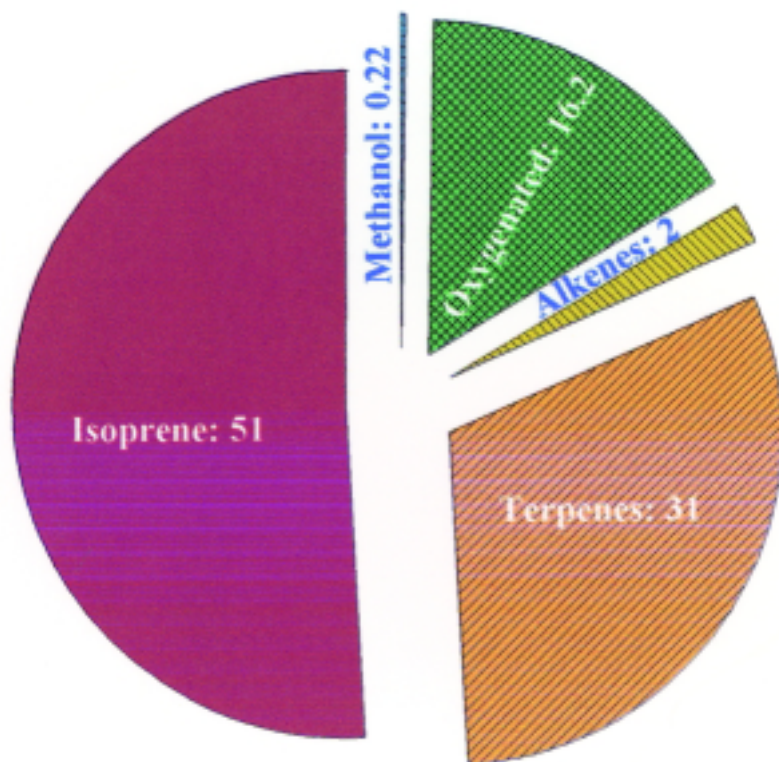
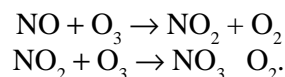


FIG. 19. North American continental biogenic NMOC emissions weighted by OH reactivity (based upon Guenther et al. 1999). Organic acids and alkanes make small percentages of the total NMOCs, each contributing 0.01% and 0.002%, respectively.

acid (HONO) (generated from the heterogeneous hydrolysis of  $\text{NO}_2$ ) and indirectly from the photolysis of HCHO, and during both daytime and nighttime from the reactions of  $\text{O}_3$  with alkenes (including biogenic alkenes such as isoprene and monoterpenes) (Paulson and Orlando 1996). Paulson and Orlando (1996) have postulated from model calculations that in both polluted and rural air masses the  $\text{O}_3 + \text{alkene}$  reactions can be a major source of OH radicals during both daytime and nighttime.

*c. Nitrate radicals in the troposphere*

The presence of NO in the troposphere from natural and anthropogenic combustion sources is followed by reactions leading to the formation of the  $\text{NO}_3$  radical (Atkinson et al. 1997):



Because  $\text{NO}_3$  radicals photolyze rapidly (with a lifetime of  $\sim 5$  s for an overhead sun) and react rapidly with NO (Atkinson et al. 1997), their concentrations are low

TABLE 2. Calculated tropospheric lifetimes for selected biogenic NMOCs with respect to gas-phase reaction with OH radicals, NO<sub>3</sub> radicals, and O<sub>3</sub>.

Biogenic NMOC	Lifetime* for reaction with		
	OH	NO <sub>3</sub>	O <sub>3</sub>
Isoprene	1.4 h	50 min	1.3 days
Camphene	2.6 h	50 min	18 days
3-carene	1.6 h	4 min	11 h
Limonene	50 min	3 min	2.0 h
Myrcene	40 min	3 min	50 min
α-pinene	2.6 h	5 min	4.6 h
β-pinene	1.8 h	13 min	1.1 days
Sabinene	1.2 h	3 min	4.6 h
β-caryophyllene	40 min	2 min	2 min
Longifolene	3.0 h	50 min	> 33 days
Methanol	12 days	1 yr	> 4.5 yr
2-methyl-3-buten-2-ol	2.1 h	4 days	1.7 days
Cis-3-hexen-1-ol	1.3 h	2.1 h	6 h
Linalool	50 min	3 min	55 min
1,8-cineole	1.0 day	270 days	> 4.5 yr
Cis-3-hexenylacetate	1.8 h	2.3 h	7 h
6-methyl-5-hepten-2-one	55 min	4 min	1.0 h
Methyl vinyl ketone	6.8 h	> 1.0 yr	3.6 days
Methacrolein	4.1 h	14 days	15 days
3-methylfuran	1.5 h	3 min	19 h
Pinonaldehyde	2.9 h	2.3 days	> 2.3 yr
Caronaldehyde	2.9 h	1.9 days	> 2.3 yr
Sabinaketone	2.3 days	130 days	> 0.9 yr
Nopinone	10 h	—	—
Camphenilone	2.3 days	—	—
4-acetyl-1-methylcyclohexene	1.1 h	3 min	2.6 h

\*With concentrations (molecule per cubic centimeter) of OH, 12-h daytime average of  $2.0 \times 10^6$ ; NO<sub>3</sub>, 12-h nighttime average of  $5 \times 10^8$ ; O<sub>3</sub>, 24-h average of  $7 \times 10^{11}$ .

during daylight hours but can increase during nighttime to concentrations up to  $\sim 1 \times 10^{10}$  molecule cm<sup>-3</sup> [a mixing ratio of 430 parts per trillion (ppt)] at ground level over continental areas (Atkinson et al. 1986; Mihelcic et al. 1993; Platt and Heintz 1994). A 12-h average nighttime concentration of  $5 \times 10^8$  molecule cm<sup>-3</sup> (20 ppt mixing ratio), uncertain to a factor of  $\sim 10$ , has been proposed as a reasonable value for lifetime calculations (Atkinson 1991).

#### 1) LIFETIMES OF BIOGENIC ORGANIC COMPOUNDS IN THE TROPOSPHERE

Rate constants for the gas-phase reactions of many biogenic NMOCs with OH radicals, NO<sub>3</sub> radicals, and O<sub>3</sub> have been measured, mostly at room temperature (Atkinson 1989, 1991, 1994, 1997; Grosjean and Grosjean 1994, 1998; Atkinson et al. 1995; Rudich et al. 1995, 1996; Grosjean et al. 1996; Smith et al. 1996; Ferronato et al. 1998; Fantechi et al. 1998a). The measured rate constants can be combined with assumed ambient tropospheric concentrations of OH radicals, NO<sub>3</sub> radicals, and O<sub>3</sub> to give the lifetimes of the NMOC with respect to each of these loss processes. The calculated lifetimes for a representative subset of biogenic NMOC are given in Table 2, which shows that many of the biogenic NMOCs are highly reactive in the troposphere, with calculated lifetimes of a few hours or less. This highly reactive nature of many of the biogenic NMOCs may explain, at least in part, observations that ambient concentrations of biogenic NMOCs, relative to an-

thropogenic NMOC concentrations, are often low or very low compared to their respective emission inventories.

It is important to recognize that ambient atmospheric concentrations of OH radicals, NO<sub>3</sub> radicals, and O<sub>3</sub> are variable, with OH and NO<sub>3</sub> radicals having pronounced diurnal concentration profiles (see, e.g., Platt and Heintz 1994; Tanner et al. 1997). Therefore, because the lifetimes given in Table 2 are inversely proportional to the OH radical, NO<sub>3</sub> radical, and O<sub>3</sub> concentrations used in the calculations, they are only approximations to the real tropospheric or boundary layer lifetimes. It is, however, clear from Table 2 that all of the biogenic NMOCs react with the OH radical, and the lifetimes with respect to reaction with the OH radical set an upper limit to the overall tropospheric lifetimes. Biogenic NMOCs containing >C=C< bonds also react with NO<sub>3</sub> radicals and O<sub>3</sub>, and these reactions must also be considered for these NMOCs. In particular, two of the sesquiterpenes for which data are available ( $\beta$ -caryophyllene and  $\alpha$ -humulene) react very rapidly with O<sub>3</sub> (Atkinson 1997) with calculated lifetimes of ~2 min at an O<sub>3</sub> mixing ratio of 30 ppb; hence if these two sesquiterpenes are emitted from vegetation they will rapidly react with O<sub>3</sub> and be present at very low concentrations in the atmosphere.

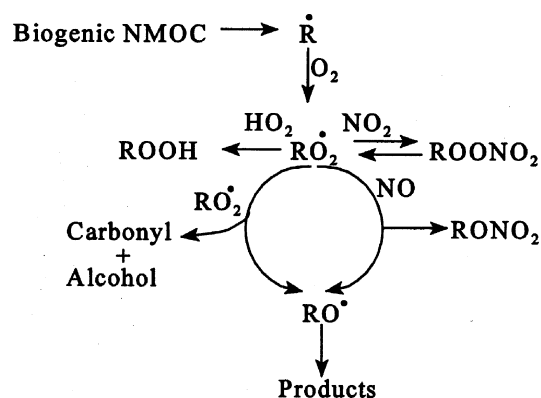
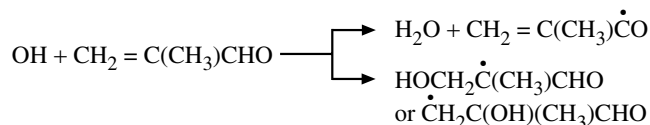
Rate constants have also been measured for a number of biogenic NMOC atmospheric reaction products, including for methyl vinyl ketone (isoprene), methacrolein (isoprene), 3-methylfuran (isoprene), camphenilone (camphene), caronaldehyde (3-carene), 4-acetyl-1-methylcyclohexene (limonene), 3-isopropenyl-6-oxo-heptanal (limonene), pinaldehyde ( $\alpha$ -pinene), nopinone ( $\beta$ -pinene), and 5-methyl-5-vinyltetrahydrofuran-2-ol (linalool) (where the precursor biogenic NMOC is given in parentheses) (Atkinson 1989, 1994; Rudich et al. 1995; Alvarado et al. 1996, 1998a; Kwok et al. 1996; Kind et al. 1996; Gierczak et al. 1997; Glasius et al. 1997; Hallquist et al. 1997; Neeb et al. 1998; Calogirou et al. 1999b). Calculated tropospheric lifetimes of selected biogenic NMOC atmospheric reaction products are also given in Table 2.

## 2) REACTION MECHANISMS AND PRODUCTS

The initial reactions of OH radicals, NO<sub>3</sub> radicals, and O<sub>3</sub> with NMOCs (including biogenic NMOC) have been elucidated over the past three decades (see, e.g., Atkinson and Arey 1998; Atkinson 2000). For the majority of biogenic NMOCs there are two general re-

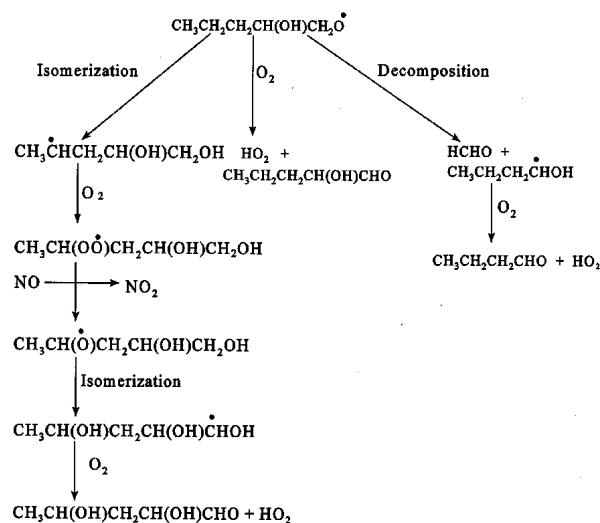
action mechanisms, involving (a) H-atom abstraction from the various C–H bonds and, to a much lesser extent, O–H bonds by OH and NO<sub>3</sub> radicals, and (b) addition of OH radicals, NO<sub>3</sub> radicals, and O<sub>3</sub> to the carbon atoms >C=C< bonds. The H-atom abstraction by OH radicals and (to a lesser extent) NO<sub>3</sub> radicals is important for alkanes and for ethers, alcohols, carbonyls, and esters not containing >C=C< bonds, but is of minor importance for isoprene, monoterpenes, and sesquiterpenes, and for alcohols, ethers, esters, and ketones containing >C=C< bonds [noting, however, that H-atom abstraction by the OH radical from the –CHO group in aldehydes is sufficiently rapid that this reaction pathway is important even for aldehydes containing >C=C< bond(s) (Atkinson 1989, 1994)]. The second general reaction mechanism involves addition of OH radicals, NO<sub>3</sub> radicals, or O<sub>3</sub> to the carbon atoms of >C=C< bonds in alkenes (e.g., isoprene, monoterpenes, and sesquiterpenes), unsaturated alcohols (e.g., *cis*-3-hexen-1-ol, linalool, and 2-methyl-3-buten-2-ol), esters (e.g., *cis*-3-hexenylacetate), and carbonyls (e.g., methacrolein, methyl vinyl ketone, and 6-methyl-5-hepten-2-one).

The H-atom abstraction reactions and the addition of OH and NO<sub>3</sub> radicals to the carbon atoms of >C=C< bonds result in the formation of an alkyl or substituted alkyl radical, R. As an example of these two reaction pathways, the reaction of the OH radical with methacrolein proceeds by both H-atom abstraction and by initial OH radical addition to the carbon atoms of the >C=C< bond:



Reaction Scheme 1

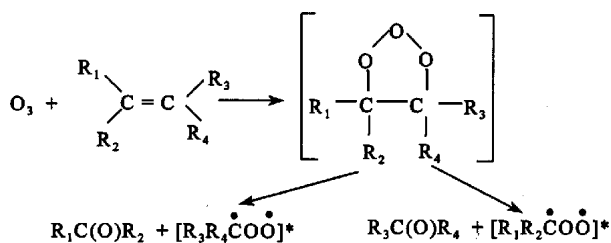
The atmospheric reactions of the alkyl or substituted-alkyl radicals formed after H-atom abstraction from C–H bonds or after OH or NO<sub>3</sub> radical addition to the carbon atoms of >C=C< bonds are shown schematically in reaction scheme 1, with the reactions proceeding through the intermediary of organic peroxy (RO<sub>2</sub>) and alkoxy (RO) radicals (Atkinson 1994, 1997, 1999). In the atmosphere, alkoxy radicals can react with O<sub>2</sub>, unimolecularly decompose, or isomerize by a 1,5-H shift through a six-membered transition state, as shown below for the CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH(OH)CH<sub>2</sub>O radical formed subsequent to OH radical addition to the internal carbon atom in 1-pentene:



Reaction Scheme 2

The reactions of O<sub>3</sub> with biogenic NMOCs containing >C=C< bonds (e.g., isoprene, monoterpenes, *cis*-3-hexen-1-ol, 2-methyl-3-buten-2-ol, and linalool) also proceed by initial O<sub>3</sub> addition to the >C=C< bond, in this case to form a primary ozonide that rapidly decomposes to, in general, two sets of carbonyl plus biradical, as shown in reaction scheme 3.

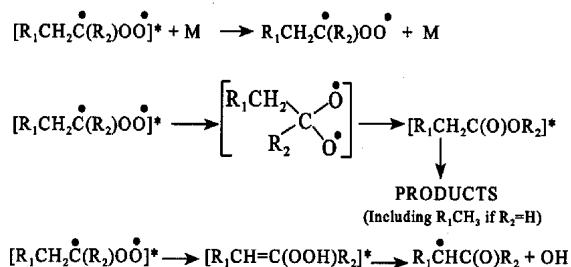
The initially energy-rich biradicals react by a number of routes, as shown later in reaction scheme 4



Reaction Scheme 3

(Atkinson 1997). These include collisional stabilization to a thermalized biradical, rearrangement to a “hot” ester followed by decomposition, and rearrangement to an energy-rich hydroperoxide that can decompose to an OH radical plus a substituted alkyl radical.

Decomposition of the biradicals to a ground-state oxygen, O(<sup>3</sup>P), atom plus a carbonyl compound has not, to date, been observed for biogenic NMOCs, although the direct formation of an epoxide has been observed from the reactions of O<sub>3</sub> with isoprene and  $\alpha$ -pinene (Paulson et al. 1992b; Atkinson et al. 1994; Alvarado et al. 1998b) with epoxide yields of ~2%–5%. It is now abundantly clear that OH radicals are formed from the reactions of O<sub>3</sub> with alkenes, including with biogenic



Reaction Scheme 4

alkenes (Paulson et al. 1992b, 1997; 1998; Atkinson et al. 1992; Chew and Atkinson 1996; Donahue et al. 1998). The measured OH radical yields from the O<sub>3</sub> reactions tend to increase with the degree of alkyl substitution around the >C=C< bond(s) (this is, in general, equivalent to the OH radical yield increasing with the reactivity of the alkene toward O<sub>3</sub>), and the measured molar OH radical yields for a few selected biogenic NMOC are isoprene, 0.25 (Atkinson et al. 1992; Paulson et al. 1998);  $\alpha$ -pinene, 0.70–0.76 (Niki et al. 1987; Chew and Atkinson 1996; Paulson et al. 1998);  $\beta$ -pinene, ~0.35 (Atkinson et al. 1992); 3-carene, limonene, myrcene, and terpinolene, ~0.8–1.0 (Atkinson et al. 1992); and *cis*-3-hexen-1-ol, ~0.25 (Atkinson et al. 1995). There are still significant uncertainties concerning the OH radical yields from many of these reactions (with uncertainties of up to a factor of ~2).

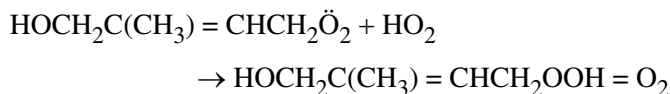
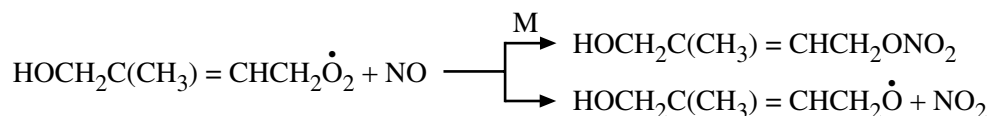
Unless the OH radicals formed from the reactions of O<sub>3</sub> with alkenes and other compounds containing >C=C< bonds are “scavenged,” laboratory studies of O<sub>3</sub> reactions will involve both OH radicals and O<sub>3</sub> and the products observed and quantified are not applicable solely to the O<sub>3</sub> reaction (see, e.g., Hakola et al. 1994).



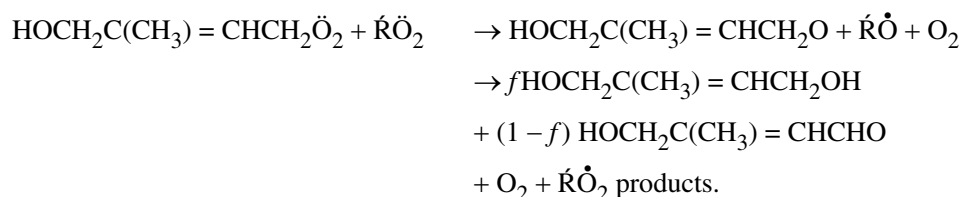
This formation of OH radicals from the reactions of  $O_3$  with alkenes and other VOCs containing  $>C=C<$  bonds may be an important additional source of OH radicals in the troposphere, and especially during nighttime (Paulson and Orlando 1996). Indeed, Paulson and Orlando (1996) have calculated that  $O_3$  + alkene reactions can provide a substantial fraction of the total OH radical production during daytime as well as nighttime in both polluted urban and “clean” rural air masses. Hydroxyl radical production from the  $O_3$  reaction depends on the ambient concentrations of the biogenic NMOC (and of  $O_3$ ), the OH radical formation yield from its reaction with  $O_3$ , and the rate constant for reaction with  $O_3$  (Paulson et al. 1998).

To date, product and mechanistic studies of the atmospherically important reactions of isoprene (Atkinson 1997, and references therein; Chen et al. 1998), several monoterpenes (with most studies emphasizing  $\alpha$ - and  $\beta$ -pinene) (Atkinson 1997, and references therein; Wängberg et al. 1997; Alvarado et al. 1998b;

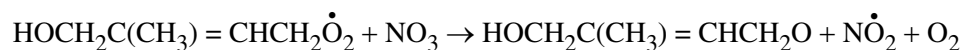
Aschmann et al. 1998; Hoffmann et al. 1998; Yu et al. 1998; Hallquist et al. 1999; Reissell et al. 1999), the sesquiterpene  $\beta$ -caryophyllene (Grosjean et al. 1993b; Shu and Atkinson 1994; Calogirou et al. 1997b), 2-methyl-3-buten-2-ol (Grosjean and Grosjean 1995; Ferronato et al. 1998; Fantechi et al. 1998b; Alvarado et al. 1999), *cis*-3-hexene-1-ol (Grosjean et al. 1993a; Atkinson et al. 1995; Aschmann et al. 1997), linalool (Atkinson et al. 1995; Calogirou et al. 1995; Shu et al. 1997), and 6-methyl-5-hepten-2-one (Grosjean et al. 1996; Smith et al. 1996) have been carried out at room temperature and atmospheric pressure of air. As evident from reaction scheme 1, the products of these reactions will depend on whether the intermediate organic peroxy ( $R_2$ ) radicals react with NO,  $HO_2$  radicals, or (especially in laboratory studies) with organic peroxy radicals. For example, for the  $HOCH_2C(CH_3)=CHCH_2O_2$  peroxy radical formed after OH radical addition to the 1-position in isoprene, these reactions are



and



And reaction with the  $NO_3$  radical during nighttime may also occur:



Based on the rate constants for the reactions of simple alkyl peroxy radicals with NO and with  $HO_2$  radicals and estimated concentrations of NO and  $HO_2$  radicals in the troposphere, the reactions of  $RO_2$  radicals

with NO will dominate for NO concentrations  $> (2-7) \times 10^8$  molecule  $cm^{-3}$  (mixing ratios  $> 10-30$  ppt), with reactions with  $HO_2$  radicals dominating at lower NO concentrations (Logan 1985).

In the troposphere, when  $\text{NO}_3$  radicals are present at significant concentrations, it is expected that NO concentrations will be low (because of the fast reactions of NO with  $\text{O}_3$  and  $\text{NO}_3$  radicals) and, hence, that the organic peroxy radicals formed after  $\text{NO}_3$  radical addition to  $>\text{C}=\text{C}<$  bonds will react with  $\text{HO}_2$ ,  $\text{NO}_3$ , and organic peroxy radicals rather than with NO.

The products observed from the reactions of OH radicals,  $\text{NO}_3$  radicals, and  $\text{O}_3$  with biogenic NMOCs are generally consistent with the reaction schemes presented above (see also Atkinson and Arey 1998; Calogirou et al. 1999a), and the individual studies should be consulted for details of the experimental methods and results obtained. The identification and quantification of many of the products observed or anticipated to be formed from these reactions (e.g., hydroxycarbonyls, dihydroxycarbonyls, hydroxynitrates, and carbonylnitrates) is a challenging problem. During the past few years significant advances in analytical methods have enabled many of these multifunctional products to be identified, and sometimes quantified (Kwok et al. 1995, 1996; Yu et al. 1995, 1998; Aschmann et al. 1997, 1998; Shu et al. 1997; Wängberg et al. 1997; Alvarado et al. 1998b; Chen et al. 1998). As one selected example of the products observed from the atmospheric reactions of biogenic NMOCs, Table 3 summarizes the products observed and their yields (when measured) from the reactions of OH radicals,  $\text{NO}_3$  radicals, and  $\text{O}_3$  with isoprene (Atkinson 1997, and references therein; Chen et al. 1998; Paulson et al. 1998). The products and mechanisms of the atmospherically important reactions of the monoterpenes are less well understood, at least in part because of the complexity of the products, difficulties in their analyses, and a lack of commercially available standards. However, progress is being made, and, for example, Aschmann et al. (1998) have observed, in addition to the previously identified and quantified pinonaldehyde from  $\alpha$ -pinene and nopinone from  $\beta$ -pinene, the formation of hydroxynitrate(s), dihydroxynitrate(s), and dihydroxycarbonyl(s) from the OH radical-initiated reactions of  $\alpha$ - and  $\beta$ -pinene in the presence of NO.

Together with studies of the atmospheric chemistry of the biogenic NMOCs emitted into the atmosphere, product and mechanistic studies have been carried out for methyl vinyl ketone, methacrolein and 3-methylfuran (Grosjean et al. 1993a; Atkinson 1994; Alvarado et al. 1996; Aschmann et al. 1996; Paulson et al. 1998) and, atmospheric reaction products of isoprene, and studies of the atmospheric reactions of

monoterpene reaction products are presently being carried out in a number of laboratories.

As noted above, the most extensive and comprehensive laboratory studies of the atmospheric chemistry of biogenic NMOCs have been carried out for isoprene and its first-generation reaction products methyl vinyl ketone, methacrolein, and 3-methylfuran (which account for a large fraction of the products of its OH radical reaction) (Martin et al. 1991; Montzka et al. 1993, 1995; Riemer et al. 1994; Yokouchi 1994; Biesenthal and Shepson 1997; Biesenthal et al. 1997, 1998; Starn et al. 1998a,b; Helmig et al. 1998). In general, the relationships observed between isoprene, methacrolein, methyl vinyl ketone, and 3-methylfuran [e.g., for the measured (methyl vinyl ketone/methacrolein), (methyl vinyl ketone + methacrolein/isoprene), and (3-methylfuran/isoprene) ratios] during daytime are consistent with OH radical reactions and atmospheric dispersion/transport (Martin et al. 1991; Montzka et al. 1993, 1995; Yokouchi 1994; Biesenthal et al. 1997, 1998; Starn et al. 1998b). As may be expected from variations in OH radical concentrations, NO concentrations [which affect the reactions of organic peroxy radicals and the OH radical concentrations (Biesenthal et al. 1998)] and atmospheric dispersion characteristics dictate the variability in ratios observed from location to location. For example, in forested areas impacted by photooxidant plumes, (methyl vinyl ketone + methacrolein)/isoprene ratios are reportedly higher than 0.8 during daytime hours whereas at night ratios can be as high as 10 (Yokouchi 1994). The dominance of daytime reaction of isoprene with OH radicals produced by photolysis of ozone and formaldehyde is often invoked to explain these observations because methacrolein is known to react more rapidly than methyl vinyl ketone with OH radicals. The strong nighttime depletion of isoprene concentrations results from both reduced emissions and reaction with  $\text{NO}_3$  radicals. It should be noted that care must be taken in interpreting methacrolein and methyl vinyl ketone data obtained in areas impacted by anthropogenic activity. Biesenthal and Shepson (1997) showed that these two isoprene oxidation products are also directly emitted in vehicle exhaust, with a methyl vinyl ketone/methacrolein emission ratio that is reasonably similar to those observed in forested (and isoprene impacted) areas.

Additionally, several studies have measured the ambient concentrations of the peroxyacyl nitrate  $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OONO}_2$  [MPAN, formed from the reaction of methacrolein with the OH radical in

the presence of  $\text{NO}_2$ , peroxyacetyl nitrate [PAN;  $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$ ] and peroxypropionyl nitrate [PPN;  $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{OONO}_2$ ], and used these data to investigate the importance of isoprene oxidation in atmospheric ozone formation (Williams et al. 1997; Nouaime et al. 1998; Roberts et al. 1998). In the interpretation of these data, MPAN was used as an indicator of isoprene photochemistry while PPN was used as an indicator of anthropogenic NMOC photochemistry (Williams et al. 1997; Roberts et al. 1998).

Figure 20 shows an example of the close correlation between isoprene and its primary oxidation products, methacrolein and methyl vinyl ketone. The data refer to samples collected in a Mediterranean ecosystem (pseudosteppe) characterized by a flux of isoprene of  $140 \text{ ng m}^{-2} \text{ s}^{-1}$  defined at the temperature and PAR levels of  $30^\circ\text{C}$  and  $1000 \mu\text{mol m}^{-2} \text{ s}^{-1}$ , respectively (Ciccioli et al. 1997). Furthermore, the generalized reaction scheme 1 indicates that the production of (peroxy) nitrates should be expected, especially when sufficient  $\text{NO}_x$  is available. Production of MPAN, an analog to the well-known anthropogenic oxidant PAN, might therefore be expected from isoprene chemistry and this compound has indeed been observed in ambient air (Roberts et al. 1998; Nouaime et al. 1998).

Difficulties exist in the detection of monoterpene oxidation products in atmospheric samples. Calogirou et al. (1997b) reported the presence at trace levels of gaseous nopinone and pinaldehyde in a rural forest area of northern Italy. However, no detectable levels of these species were measured in pine-oak forest of central Italy where high fluxes of  $\alpha$ -pinene ( $450 \text{ ng m}^{-2} \text{ s}^{-1}$ ) and  $\beta$ -pinene ( $280 \text{ ng m}^{-2} \text{ s}^{-1}$ ) were determined by trap enrichment relaxed eddy accumulation (TREA) (Valentini et al. 1997). Since atmospheric lifetimes of primary oxidation products of monoterpene compounds are only slightly shorter than those displayed by methacrolein (see Table 2), substantial removal by deposition and/or heterogeneous reaction occurring at aerosol surface has been invoked (Calogirou et al. 1997b) to explain the lack of their presence in the gas phase.

Recent field observations also suggest that a fundamental role in the for-

mation of  $\text{O}_3$  and OH radical in forests can be played by gaseous products formed by heterogeneous reactions occurring at vegetation surface. For instance, data reported in Fig. 21 show that direct emission of 6-methyl-5-hepten-2-one from orange trees is negligible when compared to the canopy fluxes measured by TREA. The origin of this gas is driven by processes occurring at the canopy level. Since both emission and flux determinations were performed during the summer season when no flowers were present, it is unlikely that gas phase oxidation of linalool is responsible for the canopy fluxes of 6-methyl-5-hepten-2-one. Laboratory experiments provide support for these observations (Fruekilde et al. 1998) that ozonolysis of epicuticular waxes acts as a strong source of 6-methyl-5-hepten-2-one, acetone, geranyl acetone, and 4-oxopentanal. Although available data refer only to five vegetation species present in the Mediterranean area, extrapolation to other European and North American plants is possible because acetone, 6-methyl-5-hepten-2-one, and geranyl acetone are all believed to originate from ozonolysis of squalene present on the leaf surface. The influence of photochemistry on carbonyl production has a strong diurnal signature, as shown in Fig. 22.

It has been known for quite some time that ozonolysis of terpenes in the atmosphere leads to particle formation (Went 1960). However, it is only recently that substantial progress has been made on the under-

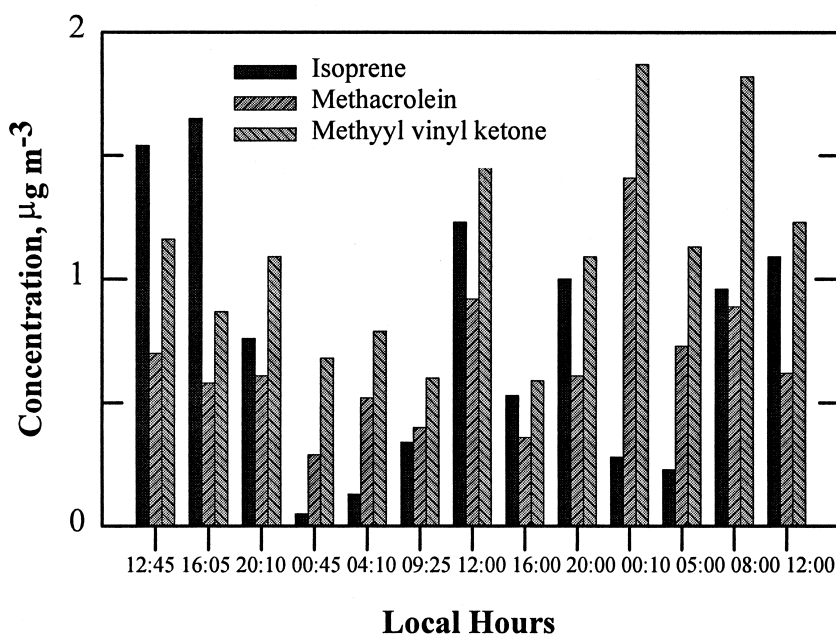


FIG. 20. Diurnal trends of isoprene, methacrolein, and methyl vinyl ketone measured on a Mediterranean pseudosteppe. Determinations were performed in Castelporziano (Italy) from 2 to 4 Jun 1993.

standing of aerosol yields and associated chemical composition from photochemical reactions of NMOCs (Hoffmann et al. 1997; Hallquist et al. 1999; Griffin et al. 1999a; Kavouras et al. 1998, 1999a,b; Yu et al. 1999a,b). Field measurements have confirmed smog-chamber studies that monoterpenes and sesquiterpenes can contribute significantly to secondary organic aerosol formation through gas/particle partitioning of their tropospheric reaction products (Mäkelä et al. 1997; Leaitch et al. 1999). Identified compounds, such as pinon acids and pinic acid, are low vapor pressure products (Pandis et al. 1991; Hoffmann et al. 1997, 1998; Griffin et al. 1999a,b). The polar products detected in particulate matter over forested areas are the same as those identified in the ozonolysis of monoterpene compounds performed in smog-chamber experiments (Yu et al. 1999a,b; Calogirou et al. 1999b). It has been hypothesized that polar compounds, such as dicarboxylic acids, may easily condense into particles as they are capable of forming dimeric compounds. Particles can then grow as soon

as the reaction proceeds because increasing amounts of polar products can be partitioned and adsorbed on the original polar nucleation sites. Despite the progresses achieved in this field, it is not yet possible to close the mass balance and new investigations are required to learn the gas to particle formation processes.

## 5. Photochemical modeling studies

Utilizing the kinetic data reported in section 4, chemical mechanisms describing the photochemistry of biogenic NMOCs have been developed (e.g., Carter and Atkinson 1996; Makar et al. 1999; Trainer et al. 1987; Stockwell et al. 1997). Such mechanisms serve to evaluate the role that natural NMOCs play in the budget of  $O_3$  and other oxidants in the troposphere. The general conclusion derived from one- (Makar et al. 1999; Trainer et al. 1987) and three-dimensional regional modeling studies (Pierce et al. 1998; Sillman et al. 1990) is that biogenic NMOCs can enhance  $O_3$  formation in environments with elevated nitrogen oxide ( $NO_x$ ) levels but the opposite effect can occur in  $NO_x$ -poor environments.

One measure of the effect of an NMOC on  $O_3$  formation is its  $O_3$  incremental reactivity (IR) (or reactivity with respect to  $O_3$  formation) (Carter 1994). The IR is determined by producing specific emission and determining  $O_3$  formation potential as established with photochemical modeling systems. Thus, an  $O_3$  IR is the change in the maximum  $O_3$  concentration divided

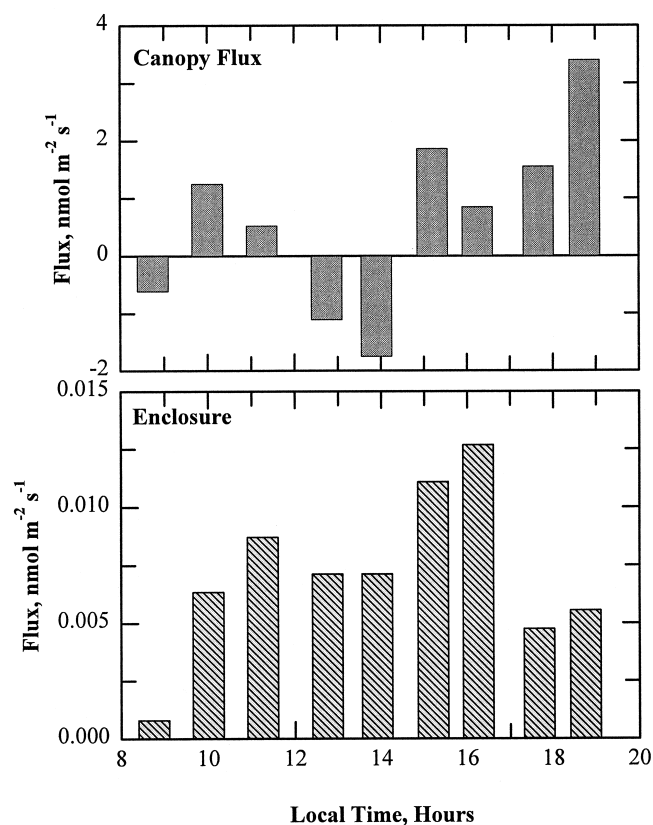


FIG. 21. Comparison between the canopy fluxes of 6-methyl-5-hepten-2-one measured by REA and the emission rates of the same compounds from tree and soil measured by enclosure techniques. Data were collected on 13 Jun 1997 in Burriana (Valencia, Spain). Fluxes are expressed per unit ground area.

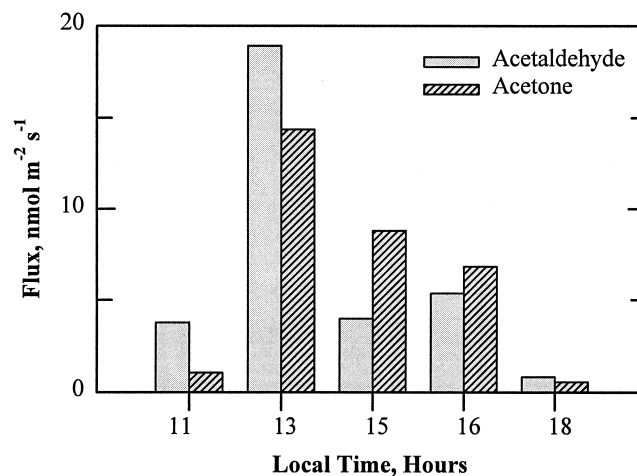


FIG. 22. Canopy fluxes of acetaldehyde and acetone from orange orchards measured by REA. Determinations were performed on 4 May 1996 in Burriana (Valencia, Spain). Fluxes are expressed per unit ground area.

by an incremental increase in the total NMOC (initial and emitted) for the chosen scenario:

$$IR = \Delta[O_3]_{\max}/\Delta[NMOC], \quad (21)$$

where IR is the  $O_3$  incremental reactivity and  $\Delta[O_3]_{\max}$  is the response to a very small change to the emitted or initial NMOC,  $\Delta[NMOC]$ . Two  $NO_x$  emission levels are typically used to calculate  $O_3$  incremental reactivities (Carter 1994). The  $NO_x$  emission rate that produces the greatest  $O_3$  maximum concentration is determined for the given NMOC and meteorological scenario. Incremental reactivities calculated for these conditions are called maximum  $O_3$  incremental reactivities (MOIR). If the  $NO_x$  emission rate increases further, a point will be found that yields the maximum incremental reactivity for a small variation in total NMOC. Incremental reactivities calculated at this  $NO_x$  emission rate for the chosen scenario are known as the maximum incremental reactivity (MIR).

A new mechanism for regional atmospheric chemistry, the Regional Atmospheric Chemistry Mechanism (RACM) (Stockwell et al. 1997), has been used to calculate MOIR and MIR values for conditions typical of rural Europe. The reaction scheme for isoprene used in RACM was based on the measurements of Paulson et al. (1992a,b). Terpenes were characterized by two lumped groups, one used to represent the reactions of monoterpenes with one double bond that was based on the chemistry of  $\alpha$ -pinene, another group for monoterpenes with two double bonds, and another based on the chemistry of *d*-limonene. There are large uncertainties in these reaction mechanisms but testing of the RACM mechanism against environmental chamber data with biogenic hydrocarbons showed that the mechanism was able to successfully reproduce the observed time-dependent  $O_3$ ,  $NO_x$ , and hydrocarbon concentrations.

The hydrocarbon scenario simulated here, Table 4, represents a moderately polluted atmosphere with NMOC emission rates typical of continental Europe. The scenario has been used in a number of previous studies (Stockwell et al. 1997; Kuhn et al. 1998). The entrainment of air from aloft and the time-dependent changes in the height of the boundary layer, humidity, and temperature were neglected because these would not be expected to greatly affect the relative magnitude of the calculated incremental reactivities. A special procedure was used to estimate the reactivity of isoprene,  $\alpha$ -pinene, and *d*-limonene because these were not included in the hydrocarbon scenario of Kuhn

et al. (1998). To calculate the incremental reactivities, four simulation scenarios were made using the following biogenic NMOC emission rates: level one,  $4.56 \times 10^{-5}$  ppb  $\text{min}^{-1}$ ; level two,  $1.14 \times 10^{-4}$  ppb  $\text{min}^{-1}$ ; level three,  $2.28 \times 10^{-4}$  ppb  $\text{min}^{-1}$ ; and level four,  $4.56 \times 10^{-4}$  ppb  $\text{min}^{-1}$ . A 5% increase for each biogenically emitted NMOC and the anthropogenic NMOC and  $NO_x$  emissions rates was introduced. The resulting MOIR and MIR values did not show any significant dependence on the base biogenic emission rate.

The results of the incremental reactivity calculation are given in Fig. 23. The MOIRs are lower than MIRs by definition and for the most reactive compounds the MIRs are about twice as great as the MOIRs. The relative values of the incremental reactivities for isoprene under these continental European conditions are in good correspondence with those for urban American regions (Russell et al. 1995; Yang et al. 1995). The incremental reactivities for isoprene are high, near those of anthropogenic alkanes and xylene. The MIR of isoprene is less than the MIR of xylene while the MOIRs are about equal.

Terpenes have not been included in previous studies of incremental reactivity (Russell et al. 1995; Yang et al. 1995). Terpenes as represented in the RACM mechanism have incremental reactivities near toluene. The MIR of *d*-limonene is greater than the MIR of toluene although the MOIR of *d*-limonene is a little lower. The MIR and MOIR of  $\alpha$ -pinene are both a little lower than those of toluene. The incremental reactivity of these terpenes is much greater than the incremental reactivities of ketones and all of the alkanes (Fig. 23).

There is much uncertainty in these calculation of these incremental reactivities for biogenic hydrocarbons. Isoprene chemistry is highly sensitive to the yield of alkyl nitrate products and these were highly uncertain (Carter and Atkinson 1997; Chen et al. 1998). PAN and related chemistry for isoprene may be incomplete because Carter and Atkinson (1997) found with a highly detailed mechanism that PAN was underpredicted in comparison with experiments containing isoprene and  $NO_x$  even though the mechanism could predict PAN formation for experiments starting with methyl vinyl ketone and  $NO_x$  or starting with methacrolein and  $NO_x$ . Although the yields of the products from isoprene chemistry, methyl vinyl ketone, methacrolein, and HCHO have been measured, the nature and yield of other unsaturated products are mostly topics of speculation. The predicted concentrations are sensitive to the yield of OH radicals from

the ozonolysis of isoprene and other unsaturated products and this is not well known. The quantum yields and absorption cross sections remain poorly known for many of the product species. The unknowns and uncertainties for the terpene mechanisms are much greater than those for isoprene. However, these results show that biogenic NMOC emissions may contribute significantly to the production of photooxidants under rural conditions typical of the regional scale.

Because of the high reactivity of isoprene (and other biogenic hydrocarbons), reactions of biogenic hydrocarbons with the OH radical will then be the dominant loss process of OH radicals and the OH radical concentration will be "regulated" by biogenic hydrocarbons. Moreover, modeling studies show that, given our current knowledge of chemistry, anthropogenic and biogenic emissions of hydrocarbons and NO<sub>x</sub> combined with prevailing meteorology, the emissions of biogenic hydrocarbons in the eastern United States, and especially in the southeastern United States, make decreasing anthropogenic NO<sub>x</sub> emissions a preferable control strategy compared to decreasing anthropogenic NMOC emissions. Based on the results obtained in the BEMA project (Seufert et al. 1997), similar considerations apply to southern Europe. Together with the importance of O<sub>3</sub>-alkene reactions as a source of OH radicals, it appears that in certain locations the chemistry of the atmospheric boundary layer is dominated by the chemistry of biogenic hydrocarbons (Makar et al. 1999).

Griffin et al. (1999b) have recently derived reactivity values for a number of biogenic hydrocarbons (monoterpenes, sesquiterpenes, linalool, and terpene-4-ol) with respect to aerosol formation. On a relative basis (*m*-xylene = 1.00), incremental aerosol formation reactivities for selected biogenic NMOC were 3-carene, 1.4; β-caryophyllene, 12; α-humulene, 13; limonene, 2.9; α-pinene, 1.0; β-pinene, 1.9; sabinene, 1.4; and terpinolene, 0.57 (Griffin et al. 1999b). In particular, these data show the high efficiencies of sesquiterpenes in forming secondary organic aerosol in the atmosphere.

## 6. Future research

The findings summarized here and elsewhere (Lerdau et al. 1997; Seufert et al. 1997; Bottenheim et al. 1998; Sharkey et al. 1999; Guenther et al. 1999; Fall 1999) show that substantial advances have been made in understanding the environmental controls on

TABLE 3. Products observed from the atmospheric reactions of isoprene.

Product	Molar yield (%)
<i>OH radical reaction (in the presence of NO)</i>	
Methyl vinyl ketone + HCHO*	32
Methacrolein + HCHO <sup>a</sup>	23
3-methylfuran	4–5
HOCH <sub>2</sub> C(CH <sub>3</sub> )=CHCHO and/or	observed
HOCH <sub>2</sub> CH=C(CH <sub>3</sub> )CHO	
CH <sub>2</sub> =C(CH <sub>2</sub> OH)CHO	observed
Organic nitrates	4.4
<i>NO<sub>3</sub> radical reaction</i>	
Methyl vinyl ketone	3.5
Methacrolein	3.5
HCHO	11
O <sub>2</sub> NOCH <sub>2</sub> C(CH <sub>3</sub> )=CHCHO and isomers	observed
O <sub>2</sub> NOCH <sub>2</sub> C(CH <sub>3</sub> )=CHCH <sub>2</sub> OH and isomers	observed
O <sub>2</sub> NOCH <sub>2</sub> C(CH <sub>3</sub> )=CHCH <sub>2</sub> OOH and isomers	observed
HOCH <sub>2</sub> C(CH <sub>3</sub> )=CHCHO and isomers	observed
<i>O<sub>2</sub> reaction</i>	
Methyl vinyl ketone	16
Methacrolein	39
HCHO	90
Epoxides	5
OH	25
O( <sup>3</sup> P)	<10

\*The cited yields refer to measured yields of methyl vinyl ketone and methacrolein. Formaldehyde is predicted to be formed as a coproduct to methyl vinyl ketone and methacrolein, and its measured yield is consistent with these expectations.

hydrocarbon emissions. However, underlying reasons as to why only certain plant species release hydrocarbon remains elusive. Continued research is necessary to understand the biochemistry of NMOCs.

Modeling systems can realistically integrate leaf-based hydrocarbon emissions to the forest ecosystem level provided that 1) active biomass distributions are adequately represented in modeling systems, and 2) the environmental forcing variables driving emissions as they vary with plant canopy depth are reliably prescribed. Further model development is required to incorporate in emission algorithms the influences of drought events, low temperature episodes observed during the middle of the growing season,

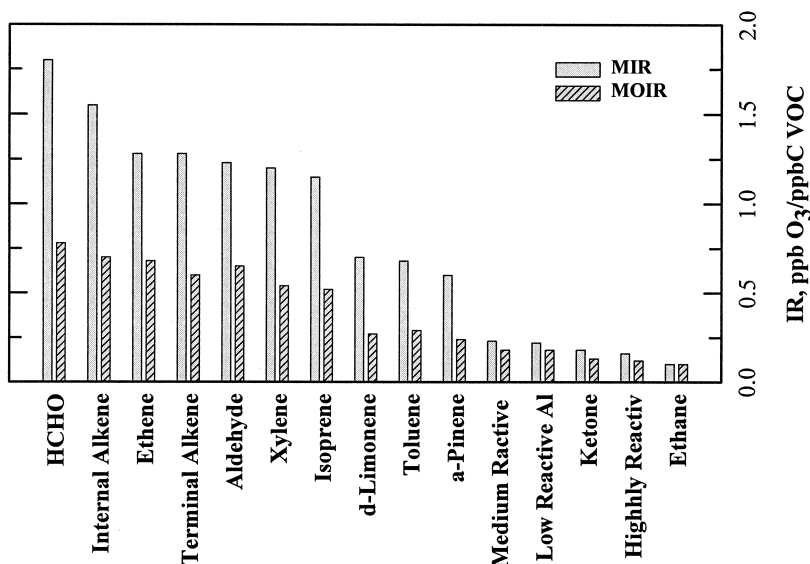


FIG. 23. Calculated incremental reactivities for NMOCs included in the RACM mechanism.

nutrient (nitrogen) status, and seasonal perturbations on emissions.

Measurements of biogenic hydrocarbon fluxes are still too labor intensive and require development of automatic in situ flux measurement systems. Such new systems will permit continuous and long-term field measurements to be made. There is a need for more long-term measurements of hydrocarbon fluxes from several forest ecosystems to quantify variations in hydrocarbon fluxes due to changes in temperature and canopy structure, and biotic (i.e., onset of emissions and leaf senescence effects) and abiotic (drought and temperature) influences on emissions. Most studies reported to date pertain to mid- and high-latitude forest ecosystems. There is a dearth of information on the hydrocarbon source strength from tropical systems.

Because many tropical forest ecosystems are physiologically active year-round or experience wet-dry season regimes, their contribution to global NMOCs is likely to be overwhelming. It is crucial to determine their contribution to the total atmospheric load of biogenic hydrocarbons. Research should initially focus on ambient concentration measurements over dominant ecosystems. Areas with large fluxes/concentrations should be studied in depth to determine ecological characteristics of these systems and to develop algorithms to simulate emissions of key compounds from key plant species. Likewise, little ecological or biogenic NMOC emission information exists at landscape scales for rangeland and arid land vegetation. In the United States and Mediterranean areas, shrub-land species are widespread and, although their biomass

density is low compared to forest ecosystems, they may emit substantial quantities of biogenic NMOCs. Most of these systems and their emissions are very poorly characterized. Further, they are often situated in areas of high photochemical potential. With increasing stringency of  $O_3$  standards in many North American and European jurisdictions, NMOC emissions from these systems will be of increasing importance to air quality modelers.

Highly detailed ecological data, including species abundance from ground surveys and spatial distribution of leaf-area indices determined from remotely sensed platforms have resulted in dramatic improvements in the accuracy of NMOC emission models for some parts

of the globe. However, for most regions of the world, appropriate data are still severely lacking. Much more detailed species classification data are needed to estimate NMOC fluxes compared with carbon dioxide, nitrogen, or water fluxes, since NMOC species and emission rates vary much more dramatically from species within a given ecosystem. Until such data are available, only crude representations of empirically derived fluxes will be possible for most areas. This is critical if we are to model the impacts of climate/chemical changes on ecosystems and land uses, since these stressors cause shifts in abundance of species and not on entire ecosystems.

In terms of the role of biogenic NMOCs in photochemistry, it seems clear that efforts to improve emission models for isoprene, terpenes, and especially oxygenated NMOCs should receive a high priority. These latter compounds typically comprise 30%–50% of NMOC inventories, yet little is known about their sources, controls, and chemistry. Recent findings indicate that anthropogenic perturbations of natural ecosystems (e.g., forest cutting) and agricultural practices (livestock grazing, crop/feed harvesting) can result in fluxes of oxygenated compounds that are comparable to isoprene fluxes from forests. The source strength of these oxygenated NMOCs needs to be quantified and their importance to regional chemical processes must be determined.

As noted in section 4, many biogenic NMOCs are highly reactive in the troposphere, with calculated chemical lifetimes of a few hours or less (depending on the actual concentrations of OH radicals,  $NO_3$  radi-

cals and O<sub>3</sub>). While the kinetics of the gas-phase reactions of biogenic NMOCs with OH radicals, NO<sub>3</sub> radicals, and O<sub>3</sub> appear to be reasonably well understood (and measurements of reaction rate constants can generally be reliably carried out), the products formed from these reactions and the detailed reaction mechanisms are much less well known. While substantial progress in elucidating the atmospheric reaction products and mechanisms has been made during the past few years, there is a continued need to develop and test new analytical methods for the identification and quantification of labile multifunctional products formed from these reactions.

The yields of aerosol formation from the reactions of terpenes, aldehydes, alcohols, and ketones need to be further quantified. Determination of sources for these compounds (primary emissions vs reaction products of other hydrocarbons) and associated impacts of aerosols on the earth's climate system require further research. There is revived interest in the role of biogenic NMOCs in haze formation. New research on mono/sesquiterpene species and fluxes is needed to support decision-making processes in this area as well. Difficulties in the parameterization of heterogeneous reactions leading to particle formation need to be further quantified. Current modeling systems can capture atmospheric chemical processing similar to those examined in smog chambers where high actinic irradiance levels and dominance of gas-phase reactants prevail. Within plant canopies, however, losses of biogenic NMOCs can take place for reactive chemical species. Thus, for short-lived chemical species, photochemical modules need to be incorporated in canopy dispersion modeling systems so that the fluxes of resulting products can be used to assess the O<sub>3</sub> formation potential.

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TABLE 4. Initial conditions for incremental reactivity calculations.

Start time (local hour)	0300
End time (local hour)	2200
Pressure (mbar)	1013.25
Temp (K)	298.15
Photolysis frequencies	1 Jul, latitude 45°
Initial concentrations	
Species	ppb
O <sub>3</sub>	50
H <sub>2</sub> O <sub>2</sub>	2.0
NO	0.2
NO <sub>2</sub>	0.5
HNO <sub>3</sub>	0.1
HCHO	1.0
CO	200
CH <sub>4</sub>	1700
H <sub>2</sub>	500
%	
H <sub>2</sub> O	1.0
O <sub>2</sub>	20.9
N <sub>2</sub>	78.1
Species emissions (ppb min <sup>-1</sup> )	
NO (MOIR)	7.51 × 10 <sup>-3</sup>
NO (MIR)	1.27 × 10 <sup>-2</sup>
SO <sub>2</sub>	5.18 × 10 <sup>-4</sup>
CO	5.65 × 10 <sup>-3</sup>
Ethane	2.41 × 10 <sup>-4</sup>
Low reactive alkane	2.94 × 10 <sup>-3</sup>
Medium reactive alkane	7.70 × 10 <sup>-4</sup>
Highly reactive alkane	4.52 × 10 <sup>-4</sup>
Ethene	4.56 × 10 <sup>-4</sup>
Internal alkene	1.88 × 10 <sup>-4</sup>
Terminal alkene	2.19 × 10 <sup>-4</sup>
Toluene	5.72 × 10 <sup>-4</sup>
Xylene	5.19 × 10 <sup>-4</sup>
HCHO	1.39 × 10 <sup>-4</sup>
Aldehyde	3.62 × 10 <sup>-5</sup>
Ketone	5.02 × 10 <sup>-4</sup>

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